Characterization of Graft Copolymers and Their Emulsifying Behavior(Dissertation_全文)

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CHARACTERIZATION OF GRAFT COPOLYMERS AND THEIR EMULSIFYING BEHAVIOR

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CONTENTS

Chapter 1. Introduction.....1

Chapter 2. Comparison of True and Apparent Graft.....7

Chapter 3. Solvent Effects on Radiation Graft Copolymerization.....20

Chapter 4. Chemical Structure of Poly(Vinyl Alcohol)-Methyl Methacrylate Graft Copolymers Prepared by Various Methods.....41

Chapter 5. Comparison of Theoretical and Experimental Results on Yield and Chemical Structure of Graft Copolymers in Radiation Grafting.....59

Chapter 6. Isolation of Graft Copolymers from Their Reaction Products.....82

Chapter 7. Emulsifying Effect of Graft Copolymer for the Homopolymer.....103

Chapter 8. Effect of Graft Copolymer on Demixing of Immiscible Polymers in Solution.....122

Chapter 9. The Formation and Flocculation of Graft Copolymer Micelles.....140

Summary.....157

List of Publications.....162

Acknowledgements.....163

CHAPTER 1

INTRODUCTION

The modification of elastomers, plastics or fibers is becoming increasingly important since the development of completely new polymers will probably diminish in importance in the future. Furthermore the type of polymers applicable to large scale practical use will become increasingly limited due to pollution problems. As a result of these recent situations one of the most important modifications is block or graft copolymerization.

The resultant block or graft copolymers can be regarded as a kind of amphiphilic compounds(1), such as synthetic surfactants and lipids in vivo, which are characterized by possessing in the same molecule two groups or sequences differing greatly in their solubility behavior. Therefore graft copolymers can be expected to exhibit emulsification or solubilization leading to formation of micelles which are colloidal particles composed of many aggregated molecules. These characteristic properties permit polymeric materials to have a high-ordered, multi-phase structure whose importance is increasingly recognized in the field of materials science. High impact polystyrene and ABS resins are typical examples of industrial success of these modified polymers.

According to Ceresa(2) and Battaerd and Tregear(3), Compagnon and Le Bras(4) in 1941 prepared a modified natural rubber by polymerizing acrylonitrile, swollen in the stabilized latex particles, with ethyl peroxide. This was the first report concerning the formation of a graft copolymer. However, it was not until 1950 that the term "graft" was adopted by Alfrey and Bandel(5). "Graft copolymer" was officially defined in 1952 by the International Union of Pure and Applied Chemistry (IUPAC). The application of radiation techniques to produce graft copolymers is generally regarded as beginning with the work by Mesrobian, Ballantine and Dienes reported at the Symposium on Macromolecular Chemistry of the IUPAC, Milan, Italy, 1954(6). Since then, the possibility of chemically combining synthetic

polymers with natural or other synthetic ones has attracted the attention of numerous workers, especially in industry. Up to the present time, over 1500 patented graft copolymers have been synthesized(3).

In spite of the large number of investigations, it is not yet obvious whether graft copolymers are capable of behaving as amphiphilic compounds and hence achieving the expected purposes. This reason may be due to the fact that most of workers have ignored fundamental studies such as the isolation of pure graft copolymer from the reaction product and its characterization. Their main efforts have been devoted towards so-called graft copolymerizations and measurements of the properties of crude grafted products usually containing a large amount of homopolymers. Battaerd and Tregear(3) stated in their book as follows; "in a great many reviews, authors are either optimistic and claim the field of graft copolymers to be a panacea for tailor-made polymers, or bluntly state that grafts behave as the blend of the corresponding homopolymers and therefore are not a particularly exciting exercise." Regretfully, such simplistic reviews often appear even at this time. Since modern anionic synthetic methods have opened a way to prepare relatively well-defined block or graft copolymers, data on the behavior specific to block and graft copolymers have been accumulated and thus the latter opinion has not been fully justified. It should be possible to confirm the validity of the former claim, especially in the field of radiation grafting since the technique is characterized by the possibility of wide variations in backbone-branch combinations.

The objective of this dissertation is to clarify the characteristics of graft copolymer through systematic investigations on the synthesis, characterization and physicochemical properties. To achieve this end, the graft copolymerizations of styrene and methyl methacrylate(MMA) onto poly(vinyl alcohol) (PVA) were carried out mainly by the gamma-ray irradiation technique. PVA-styrene or PVA-MMA graft copolymers were isolated from the reaction products by alternate extraction, which has been already successfully used by Stannett and his co-workers(7,8) and us(9,

10). After isolation, the graft copolymers were characterized and the emulsifying behavior was investigated.

Chapters 2 and 3 are mainly devoted to the polymerization mechanism of radiation grafting. In grafting reactions, especially radiation grafting, solvents such as water and methanol are frequently used and the product is extracted with a solvent for the homopolymer corresponding to the graft side chain. However, the question arises whether all the nongrafted homopolymers are really extracted or not. In addition the role of solvent is not clear. Therefore, we carried out the grafting of MMA onto dry or water-swollen PVA films in the presence of various concentrations of methanol mainly by the mutual irradiation technique and have attempted to isolate pure PVA-MMA graft copolymer from the reaction product by the alternate extraction method. In Chapter 2, the apparent grafting yield after a conventional extraction is compared with the true grafting result. It is pointed out that the former yield has little significance as the basis for discussing the mechanism of grafting because of significant differences which were obtained. The dependences of the true yield and branch length on the monomer concentration and the degree of swelling of the film are also discussed. In Chapter 3, the effects of methanol on the grafting of styrene or MMA onto PVA films are discussed on the basis of the weight increase of the films, the monomer conversions and the molecular weights of the homopolymers. The effects of chain transfer agents are also discussed in a similar way.

Chapters 4 and 5 are concerned with the characterization of graft copolymers prepared by various methods. Hitherto very little effort has been devoted to the characterization of graft copolymers, in particular the synthesis of graft copolymers suitable for the fundamental investigation of their properties. We intended to prepare graft copolymers whose branch length is comparable to that of backbone by employing chain transfer agents. In Chapter 4, the syntheses of PVA-MMA graft copolymers by mutual irradiation, pre-irradiation, catalytic method with potassium persulfate and without initiator are described and the yield as

well as the chemical structure of the graft copolymers obtained are compared. In Chapter 5, the fundamental quantities in graft copolymerization, such as the yield and chemical structure of graft copolymers, are calculated as a function of the probability of branch formation from the monomer residue of the mother polymers. The theoretical and observed results are compared with each other for the radiation graftings of styrene or MMA onto PVA, cellulose poly(ethylene terephthalate) and nylon. Some attempts to increase the number of branches are also described.

Chapter 6 is devoted to general discussions on various isolation methods of graft copolymer from the reaction product by referring to the investigations of the previous chapters. It is concluded that the difficulty in the isolation process is mainly due to the amphiphilic property of the graft copolymer. It is hoped that these discussions will provide useful suggestions for workers in the field of graft copolymers. Numerous interesting properties of the graft copolymers were also found during the process of isolation.

Chapters 7, 8 and 9 are concerned with studies on the amphiphilic behavior of the well-defined graft copolymers from PVA or poly(vinyl acetate) (PVAC). Merrett(11) first observed the formation of a stable colloidal sol during fractionation of a grafted product and interpreted the phenomenon as an effect of the co-existing graft copolymer. On the other hand, Hughes and Brown(12) found that solutions of polystyrene-poly(ethyl acrylate) mixture prepared from the product of polymerization of styrene in poly(ethyl acrylate) emulsion apparently consisted of a single hazy phase, while the physical mixture of these homopolymers separated into two distinct layers when dissolved in common solvents. A similar phenomenon was also reported by Molau(13) in several polymer-polymer systems. He concluded that this must be due to the emulsifying ability of a graft copolymer which would have been formed during polymerization and accumulated on the surface of droplets of polymer solution. However these phenomena have not been investigated quantitatively. It seems of interest, therefore, to study how much graft copolymer is needed to emulsify a given amount of homopolymer and whether the graft copolymer is capable of controlling the size of micelles formed at the emulsi-

fications. In Chapter 7, the effect of PVA-MMA graft copolymer on the protection of homoPMMA against precipitation from solution caused by the addition of a selective precipitant is discussed. A stable emulsion is shown to be formed as a result of the protection of homopolymer against precipitation. In Chapter 8, the effect of PVAC-styrene graft copolymer on the demixing of immiscible PVAC-PS solutions and the structure of the resulting emulsion are discussed. It will be suggested from these studies that the graft copolymer is able to play an important role in a composite system even when the amount present is relatively small.

Investigations on the mechanisms of the formation and stabilition of graft copolymer micelles are essential in order to clarify the emulsifying ability of graft copolymer, especially the ability of controlling the size of micelles. Thus, in Chapter 9, the aggregation process of the pure graft copolymer is followed by turbidimetry and the critical points of the formation and flocculation of graft copolymer micelles are determined. On the basis of these results the stability of the micelles is explained in terms of the theory of nonionic polymeric dispersants(14,15).

REFERENCES

1) P. A. Winsor, Chem. Rev., 68, 1 (1968).
2) R. J. Ceresa, Block and Graft Copolymers, Butterworths, London, 1962.
3) H. A. J. Battaerd and G. W. Tregear, Graft Copolymers, Interscience, New York, 1967.
4) P. Compagnon and J. Le Bras, C. R. Acad. Sci., Paris, 212, 616 (1941); Rev. Gén. Caoutch., 18, 89 (1941).
5) T. Alfrey and D. Bandel, Paper presented at the 118th Am. Chem. Soc. Meeting, Chicago, 1950.
6) D. S. Ballantine, A. Glines, D. J. Metz, J. Behr, R. B. Mesrobian, and A. J. Restaino, J. Polymer Sci., 19, 219 (1956).

7) H. Yasuda, J. A. Wray, and V. Stannett, J. Polymer Sci., C, 2, 387 (1963).
8) H. A. Ende and V. Stannett, J. Polymer Sci., A, 2, 4047 (1964).
9) I. Sakurada, Y. Ikada, and Y. Uesaki, Bull. Inst. Chem. Res., Kyoto Univ., 47, 49 (1969).
10) I. Sakurada, Y. Ikada, and F. Horii, Bull. Inst. Chem. Res., Kyoto Univ., 47, 58(1969).
11) F. M. Merrett, Trans. Faraday Soc., 50, 759 (1954); Ric. Sci., 25, 279 (1955).
12) L. J. Hughes and G. L. Brown, J. Appl. Polymer Sci., 7, 59 (1963).
13) G. E. Molau, J. Polymer Sci., A, 3, 1267, 4235 (1965).
14) E. W. Fischer, Kolloid-Z., 160, 120 (1958).
15) D. J. Meier, J. Phys. Chem., 71, 1861 (1967).

CHAPTER 2

COMPARISON OF TRUE AND APPARENT GRAFT

INTRODUCTION

Grafting, especially radiation-induced grafting is often carried out in a heterogeneous system. The product is separated after the reaction and subjected to extraction with a solvent for the homopolymer constituting the graft branch. Percent weight increase is conventionally called "percent graft". But the question arises whether all nongrafted homopolymers are really extracted or not. It is possible that a fraction of the homopolymer formed in the matrix of substrate polymer is occluded in such a state that the extraction is hindered.

Conventional or apparent percent graft is of practical importance, for example, for the modification of fiber or film properties. So long as the branch polymer is insoluble in the solvent, the problem whether the so-called graft branch molecule is really connected with its one end to the backbone or not, does not play a significant role in the modification of properties. The important thing is that the polymer is so intimately mixed with the backbone polymer as if it were grafted. Even when a graft copolymer is used after bringing it into concentrated solution or molten state, apparent graft seems to be of great value, because the presence of true graft copolymer may help intimate mixing of the two homopolymers as shown in Chapter 8. However, from the scientific point of view, it is necessary to know the true percent graft. As will be shown later in detail, a product of 100 % apparent graft often has a value of less than 10 % true graft. It is essentially necessary to know the true percent graft for discussing the mechanism or kinetics of grafting.

It is expected that some more homopolymer will be extracted, if we extract the unreacted substrate polymer after extraction of the homopolymer. By continuing such an alternate extraction until no more homopolymer and substrate polymer can be extracted, it is able to obtain the true graft copolymer. Stannett and collaborators(1) have carried out such an experiment with cellulose

acetate-styrene, and showed the alternate extraction method to be adequate for the analysis of grafting reaction products. Since then the alternate extraction has been widely adopted by Stannett and other investigators to obtain true graft copolymers(2-8).

The main purpose of this chapter is to compare the true and apparent percent graft based on the alternate extraction method for the poly(vinyl alcohol)(PVA)-methyl methacrylate(MMA) grafting system. We will also discuss briefly the chemical structure of the graft copolymer.

EXPERIMENTAL

1. Grafting

Unfractionated PVA with a viscosity-average molecular weight of 90,200 was thoroughly hydrolyzed and purified by Soxhlet extraction with methanol. Films were prepared from the purified PVA by casting 6 % aqueous solution on glass plates so as to have a thickness of 0.1 mm and dried under a reduced pressure at 50°C. In the case of grafting by mutual irradiation technique, strips of dry or water-swollen films were immersed in a monomer-methanol mixture, degassed by repeated cycles of freezing-thawing, and then irradiated at 50°C with gamma-rays to a dose of 9.0×10^4r or 2.4×10^5r, where the dose rates were 0.6 or 1.0×10^4r/h. The water-swollen films with higher degrees of swelling(DS) were obtained by immersing dry films in pure water at 25°C and those with lower DS in water-methanol(or acetone) mixture at 50°C. In this chapter the DS is defined to be gram water contained in one gram PVA film; the calculation of the water content was carried out with the assumption that the weight fraction of water of the liquid in the swollen film is the same as that of the initial swelling mixture.

2. Isolation of graft copolymers

Homopolymer formed in the outer solution and loosely included in the films was removed by immersing the whole reaction products in a large amount of benzene at 80°C, till no more extractable polymer was present, and the apparent percent graft was calculated from the weight increase of the films. When acetone is used for the

extraction we find usually a higher value of the apparent percent graft. Unreacted PVA backbone was extracted with a water-n-propanol(75:25) mixture, which is known to be a better solvent for PVA than water. The extraction of unreacted PVA and homoPMMA was repeated alternately till no more polymer was detected by evaporation of the solvents from the extracts, and the residue was regarded to be the pure graft copolymer. The extracted solutions were in every case transparent, and it was confirmed from infrared spectroscopy that the extracted polymers contained no appreciable amount of the other polymer component.

In order to reduce the time consumed for the isolation of the graft copolymer, we tried also selective precipitation of the graft copolymer by addition of a selective precipitant such as water or acetone to dimethyl sulfoxide solution of the whole reaction products, but clear phase-separation was not observed, which took place, on the contrary, for the solution prepared from the blend of both homopolymers. In the case of grafting products the solution became always milky by the addition of a precipitant. A further study given in Chapter 7 reveals that this phenomenon appears as a result of a protection effect of a coexisting graft copolymer against the precipitation of the homopolymer.

The apparent and true percent graft are defined as follows:

$$\text{app. percent graft} = \frac{\text{wt. increase after conventional extraction}}{\text{weight of starting PVA}} \times 100 \quad (2\text{-}1)$$

$$\text{true percent graft} = \frac{\text{wt. of branch after complete extraction}}{\text{weight of starting PVA}} \times 100 \quad (2\text{-}2)$$

3. Determination of chemical composition of graft copolymer

For the determination of the composition, the true graft copolymer was completely acetylated and the acetyl content was determined by hydrolysis. The detailed conditions of the acetylation

and hydrolysis were described elsewhere(9). The fraction of grafted PVA was calculated from the composition and the amount of the true graft copolymer.

RESULTS AND DISCUSSION

1. Comparison of the true and apparent percent graft

Table 2-1 shows the result of grafting of MMA onto dry PVA film; the table contains not only the true and apparent percent graft, and fraction of grafted PVA, but also molecular weight of the branch and number of branches. The last two items will be discussed later.

Table 2-1. Mutual grafting of MMA onto dry PVA film with MMA-methanol, Dose = 9.0×10^4r

Methanol(Vol.%)	10	30	50	70	80	90
Percent graft app.(A)	3	74	305	160	201	136
Percent graft true(B)	0	43	97	84	106	70
Fraction of true graft(B/A)	—	0.58	0.32	0.53	0.53	0.52
Fraction of PVA grafted	—	0.06	0.11	0.15	0.16	0.06
Mol.wt.of branch, $M_b \times 10^{-6}$	4.31	3.68	4.72	2.00	1.33	—
Nr. of branch[a], $B/M_b \times 10^5$	—	1.2	2.1	4.2	8.0	—

a) Nr. in mole per 100g starting PVA

From Table 2-1 it is seen that there is a considerably great difference between the true and apparent percent graft. The fraction of true graft is about 0.5. A similar but less prominent difference was also observed by Stannett et al.(3) When the grafting mixture contains no or less than 10 % methanol, grafting does not occur, but with increasing content of methanol the per-

cent graft increases, passes a maximum and then decreases. We will return to the problem of the percent graft in dependence on methanol content.

The results obtained in the grafting onto swollen films are given in Tables 2-2 to 2-4. It is seen from the tables that the apparent percent graft increases, especially when the methanol content is low, with an increasing amount of water in the swollen film. On the other hand the true percent graft increases only a little by swelling of the film, in some cases it decreases therefore the fraction of true graft is in most cases less than 0.1.

Table 2-2. Mutual grafting of MMA onto swollen PVA film(DS = 0.66) with MMA-methanol, Dose = 2.4×10^5r

Methanol(Vol.%)	0	20	40	60	80
Percent graft app.(A)	15	397	648	1,150	313
true(B)	—	29	13	36	49
Fraction of true graft(B/A)	—	0.07	0.02	0.03	0.16
Fraction of PVA grafted	0.01	0.04	0.02	0.05	0.04
Mol.wt.of branch, $M_b \times 10^{-6}$	1.29	1.18	1.02	0.66	0.64
Nr. of branch, $B/M_b \times 10^5$	—	2.5	1.3	5.5	7.7

This observation is very important. To achieve a high degree of grafting, pre-swelling of the substrate polymer is a generally adopted technique; it is true that by this technique a high apparent percent graft is effected, but the pre-swelling favors the true graft only a little. By the pre-swelling the diffusion of monomer into film becomes easier and the monomer in the film

Table 2-3. Mutual grafting of MMA onto swollen PVA film (DS = 1.2) with MMA-methanol, Dose = 9.0×10^4r

Methanol(Vol.%)	0	20	40	60	80
Percent graft app.(A)	1,380	1,110	1,094	817	289
true(B)	202	128	98	113	101
Fraction of true graft(B/A)	0.15	0.12	0.09	0.14	0.35
Fraction of PVA grafted	0.11	0.07	0.06	0.09	0.12
Mol.wt.of branch, $M_b \times 10^{-6}$	4.16	3.52	3.00	2.16	1.60
Nr. of branch, $B/M_b \times 10^5$	4.9	3.6	3.3	5.2	6.3

Table 2-4. Mutual grafting of MMA onto swollen PVA film (DS = 2.3) with MMA- methanol, Dose = 9.0×10^4r.

Methanol(Vol.%)	0	20	40	60	80
Percent graft app.(A)	2,000	1,670	1,252	1,150	254
true(B)	159	118	102	101	78
Fraction of true graft(B/A)	0.08	0.07	0.08	0.09	0.31
Fraction of PVA grafted	0.11	0.09	0.08	0.06	0.07
Mol.wt.of branch, $M_b \times 10^{-6}$	3.89	3.34	2.62	2.02	1.26
Nr. of branch, $B/M_b \times 10^5$	4.1	3.5	3.9	5.0	6.2

is polymerized mostly initiated by monomer radicals or solvent radicals independent of substrate radicals. In the case of dry film, monomer diffusion is very difficult, so that the concentration of solvent and monomer radicals may not be so much higher than that of the substrate radicals, which initiate polymerization to effect true grafting.

In place of methanol which is a nonsolvent for PMMA and was employed in the foregoing experiments, acetone, a solvent for PMMA, was used; the results are shown in Table 2-5.

Table 2-5. Mutual grafting of MMA onto swollen PVA film (DS = 0.92) with MMA-acetone, Dose = 2.4×10^5r

Acetone (Vol.%)	0	20	40	60	80
Percent graft app.(A)	35	157	79	121	42
true(B)	12	30	29	35	20
Fraction of true graft(B/A)	0.34	0.19	0.37	0.29	0.48
Fraction of PVA grafted	0.02	0.03	0.02	0.03	0.02
Mol.wt.of branch, $M_b \times 10^{-6}$	1.89	1.08	1.63	1.47	1.29
Nr. of branch, $B/M_b \times 10^5$	0.63	2.8	1.8	2.4	1.6

There is no essential difference between methanol and acetone. In this case the apparent percent graft was rather low and the true one somewhat high. This may be attributed to the fact that acetone is a poorer swelling agent to PVA than methanol.

Pre-irradiation is a technique which seems to be very suitable to effect the true grafting. Therefore a series of experiments of grafting was carried out with this technique. Dry films were irradiated in the presence of air without moisture at 25°C to a dose of 1.0×10^6r at a dose rate of 0.68×10^4r/h, and then

transferred into ampoules, to which the monomer mixture was added. After thorough degassing, they were sealed and kept at 50°C for 24hrs to proceed with the grafting. The results are shown in Table 2-6.

Table 2-6. Pre-irradiation grafting of MMA onto dry PVA film with MMA-methanol, Dose = 1.0×10^6r

Methanol(Vol.%)	20	40	50	60	80	90
Percent graft						
app.(A)	20	522	841	836	954	571
true(B)	10	238	312	300	245	191
Fraction of true graft(B/A)	0.50	0.46	0.37	0.36	0.26	0.34
Graft efficiency(%)						
app.	11	80	84	90	96	98
true	3	38	36	35	26	34

It is seen from the table that not only the apparent but also the true percent graft is very high as was expected. A value of 300 percent true graft is the highest value found in our experiments. Concerning the graft efficiency it was found that at higher methanol concentrations the value is about 100 % for the apparent graft in accordance with observations of various researchers, but that for the true graft is much smaller and about 1/3 of the former value. Such a rather low value was also reported by Munari et al.(10) at vacuum pre-irradiation grafting of pure styrene onto cellulose diacetate. The low graft efficiency at pre-irradiation grafting may be attributed largely to the chain transfer of growing radicals to the monomer.

2. Molecular weight of branch

Now we wish to discuss the molecular weight and number of graft branches. It has been often pointed out that the molecular weight of graft branches is essentially the same as that of homopolymer formed in the substrate matrix. That this is true also

for the case of the grafting of MMA onto PVA is shown in Table 2-7.

Table 2-7. Molecular weight of graft branch and homopolymer formed in polymer matrix

Grafting method	$M_n \times 10^{-5}$		Ref.
	Branch	Homopolymer	
Pre-irradiation	4.42	4.63	Chapter 4
Pre-irradiation	4.35	3.9	(11)
Pre-irradiation[a)]	62[b)]	68[b)]	(12)
Pre-irradiation	4.4	4.5	(12)
Mutual irradiation	1.81	1.77	Chapter 4
Catalytic(KPS)	1.46	1.04, 1.67	Chapter 4

a) All graftings except this one were carried out in the presence of trichloroethylene as a transfer agent.
b) These molecular weights are viscosity-average.

Therefore, in the present case molecular weight determination was not carried out for separated branches, but viscometric estimation was carried out for homopolymers formed in the matrix by using the following equation(13):

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_v^{0.76} \qquad (30^{\circ}C, \text{ in benzene})$$

The molecular weights of the homopolymers obtained in the present work are in most cases higher than the upper limit of the above equation, beyond which there is no experimental evidence that the equation is applicable. Therefore, it should be stressed that only a qualitative meaning should be attributed to those values obtained by the above equation. Molecular weights of branch M_b, shown in Tables 2-1 to 2-5 represent these values.

Molecular weights of branches for PVA's of different degrees of swelling in dependence on methanol content of the grafting mixture are summarized in Fig. 2-1.

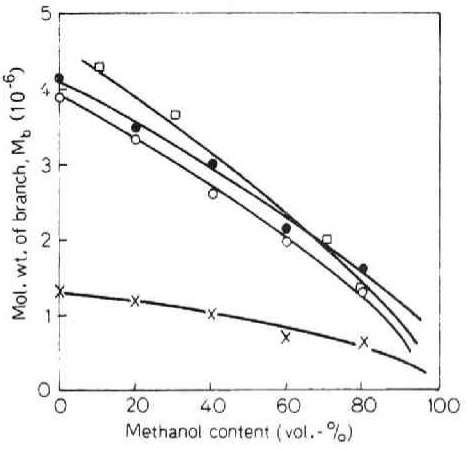


Fig. 2-1. Molecular weight of branch vs. methanol content of grafting mixture at different degrees of swelling (DS).

□ : DS = 0

X : DS = 0.66

● : DS = 1.2

○ : DS = 2.3

As clearly seen from Fig. 2-1, in all cases the molecular weight of branches decreases monotonously with increasing content of methanol. Several reasons may be ascribed to the monotonous decrease of branch length with methanol; for instance, the decrease of monomer concentration with methanol, the chain transfer to methanol, the influence of methanol radicals produced by direct irradiation etc. Concerning the role of methanol at the grafting we will discuss in detail in Chapter 3.

It is interesting to point out here that Tables 2-1 and 2-2 show maxima of apparent percent graft at a methanol content of 50~60 %. Such a phenomenon is often ascribed to a so-called gel-effect of methanol, since methanol, a precipitant for homopolymer(PMMA), may disturb termination of growing chains, resulting in a higher degree of polymerization of the graft chains(3, 14). However, the present result indicates that the maxima of apparent percent graft cannot be attributed merely to the gel-effect. A remark should be given here that we have newly found that the gel-effect really plays an important role when styrene is grafted onto PVA, as will be shown in Chapter 3.

3. Estimation of the number of branches

The number of branches may be expressed by various ways, but we wish to adopt in the present work an expression of "number of branches per 100 g starting PVA in mole", which is equal to B/M_b. The calculated number was already shown in Tables 2-1 to

2-5. Fig. 2-2 shows again the number in dependence on the methanol content for the grafting to PVA films of various degrees of swelling.

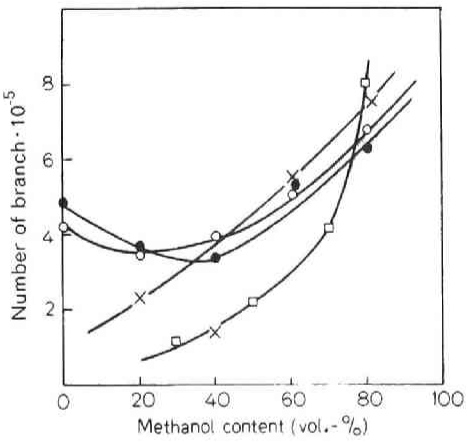


Fig. 2-2. Number of branches vs. methanol content of grafting mixture at different degrees of swelling (DS).

□ : DS = 0

× : DS = 0.66

● : DS = 1.2

○ : DS = 2.3

As Fig. 2-2 shows, in two series of experiments for low amount of water in the swollen film, the number of branches increases rapidly with the increase of the methanol content. It means probably that the diffusion of monomer into films is more and more accelerated by the increasing content of the methanol of the grafting mixture, and the initiation of polymerization can take place at radicals formed on the backbone of PVA molecules before decay.

When the amount of water in the swollen films is high, the number of branches decreases a little at first and then increases with increasing content of methanol. The first decrease may be explained by an assumption that water in PVA film is expelled by methanol to reduce the diffusibility of monomer. When the methanol content of the grafting mixture is high, the pre-swelling of film plays only an unimportant role, and the number of branches becomes almost independent of the degree of pre-swelling.

The above number of branches is expressed as a number per 100 g starting PVA, from which only a fraction has taken part really in the grafting. By dividing the number of branches per 100 g starting PVA in mole by the fraction of grafted PVA, one

obtains the number of branches per 100 g grafted PVA. By multiplying the latter number by 902 (the viscosity-average molecular weight of mother PVA is 90,200) one arrives finally at a number of branches per one grafted PVA molecule.

The above-mentioned way of calculation is theoretically correct, but there are many experimental uncertainties;

1) only viscosity-average molecular weight of the mother PVA is known; but in this case the number-average molecular weight is necessary for the calculation,
2) the molecular weight of branch is also viscosity-average, which was calculated by an equation, in most cases from a very large limiting viscosity number at which the applicability of the equation is not yet supported with experiments,
3) the value of the fraction of grafted PVA may have comparatively large experimental error.

Notwithstanding the uncertainties, calculation was carried out to find the order of magnitude of the number of branches per one grafted PVA molecule. Twenty three experimental results shown in Tables 2-1 - 2-5 gave numbers which lay between 0.2 and 1.70. The average number was 0.64, a number which is nearly equal to one. We believe, in spite of the uncertainties, that the value is very reasonable. The number of grafted branches per total starting substrate polymer is often estimated by various workers(14 - 17), but there is no calculation of branch numbers per one grafted substrate polymer except that of Stannett et al.(3), who showed the number to be approximately one.

To arrive at a reliable result it is more necessary than anything else to prepare copolymers whose branch length is about one tenth of that of copolymers mentioned in the present work and find number-average molecular weights of mother PVA and branch. As will be shown in Chapter 4, we have carried out grafting in the presence of a chain transfer agent, trichloroethylene, and osmometric molecular weight determinations. And we have succeeded to show that the separated true graft copolymer molecule really consists of one branch and one mother PVA molecule.

REFERENCES

1) H. Yasuda, J.A. Nray and V. Stannett, J. Polymer Sci., C, 2, 387 (1963).
2) V. Stannett, J.D. Wellons, and H. Yasuda, J. Polymer Sci., C, 4, 551 (1963).
3) J. D. Wellons, J. L. Williams, and V. Stannett, J. Polymer Sci., A-1, 5, 1341 (1967).
4) J. D. Wellons, A. Schindler, and V. Stannett, Polymer(London), 5, 499 (1964).
5) H. Sumitomo, S. Takakura, and Y. Hachihama, J. Chem. Soc. Japan, Ind. Chem. Sect.(Kōgyō Kagaku Zasshi), 66, 269 (1963).
6) H. Sumitomo and Y. Hachihama, J. Chem. Soc. Japan, Ind. Chem. Sect.(Kōgyō Kagaku Zasshi), 66, 1508 (1963).
7) C. J. Hamburger, J. Polymer Sci., A-1, 7, 1023 (1969).
8) E. E. Magat, I. K. Miller, D. Tanner, and J. Zimmerman, J. Polymer Sci., C 4, 615 (1963).
9) I. Sakurada, S. Matsuzawa, and Y. Kubota, Makromol. Chem., 69, 115 (1963).
10) S. Munari, G. Tealdo, and C. Rossi, Internat. Symp. Macromol. Chem., Budapest, 1969, Preprint 9/45, p. 351.
11) I. Sakurada, Y. Ikada, and Y. Uesaki, Bull. Inst. Chem. Res., Kyoto Univ., 47, 49 (1969).
12) I. Sakurada, Y. Ikada, and Y. Uesaki, Bull. Inst. Chem. Res., Kyoto Univ., 45, 1 (1967).
13) T. G. Fox, T. B. Kinsinger, H. F. Mason, and E. M. Schuele, Polymer (London), 3, 71 (1962).
14) R. Y.-M. Huang, J. Appl. Polymer Sci., 10, 325 (1966).
15) R. Y.-M. Huang, and P. Chandramouli, J. Appl. Polymer Sci., 12, 2549 (1968).
16) R. Y.-M. Huang, and P. Chandramouli, J. Polymer Sci., A-1, 7, 1393 (1969).
17) J. C. Arthur and D. J. Daigle, Textile Res. J., 34, 653 (1964)

CHAPTER 3

SOLVENT EFFECTS ON RADIATION GRAFT COPOLYMERIZATION

INTRODUCTION

The radiation graft copolymerizations which proceed heterogeneously in a substrate matrix are generally performed with the use of solvents (often named swelling agent) (1). It is expected that they accelerate the diffusion of monomer into the substrate matrix and hence increase the rate of grafting. Surely this is the strongest reason to use the solvents for the grafting. However it should be also noted that the solvent can affect the grafting, further behaving, for example, as a diluent of monomer, a chain transfer agent, and either a good solvent or non-solvent of growing polymer chains. This variety of the solvent effects makes the kinetic study of grafting much difficult.

From a view point of the solvent effect, the radiation graft copolymerization can be regarded as a matrix or heterogeneous polymerization(2) and it is not always necessary to distinguish between the grafted branch polymer and the non-grafted homopolymer which is produced in a large amount in the matrix. Therefore, in the present work the homopolymer produced during the grafting was not separated from the true graft copolymer unless the chemical structure of the graft copolymer had to be determined. Since the chain transfer agent is known to behave peculiarly in the heterogeneous polymerization(2,3), the effects were also discussed in some detail.

EXPERIMENTAL

1) Graft copolymerization

The graft copolymerization onto PVA films was carried out both with a mutual irradiation and a pre-irradiation method. In the latter grafting, dry films of 0.05 mm thickness were irradiated in the presence of air at room temperature with gamma-rays from a Co-60 source. The irradiated films were transferred into an ampoule and then a monomer-swelling agent mixture, in some

cases, containing a small amount of a chain transfer agent, was sufficiently added to the ampoule so as to immerse the films. After the ampoule was degassed by freezing and thawing, and sealed, the graft copolymerization was carried out in a water bath kept at 50°C under incessant rotation of the sealed ampoule.

The mutual irradiation grafting was carried out in the similar way as the pre-irradiation grafting except that dry or water-swollen films were irradiated simultaneously with the monomer solution in a degassed ampoule with gamma-rays.

2) Conventional polymerization

Catalytic polymerization of styrene was carried out at 50°C in methanol solution in the presence of carbon tetrachloride (CCl_4) (styrene : methanol = 40 : 60 by volume) by using α,α'-azobisisobutyronitrile (AIBN) as an initiator.

3) Removal of homopolymers

After the graft copolymerization, the whole graft products were placed in plenty of benzene at room temperature and the homopolymer formed in the outer solution and adsorbed on the surface of the films was removed. The weight increase was calculated from the weight difference of original and graft films. When the chain transfer agent was present in the monomer mixture, the graft films were at first soaked in water to prevent the eventual crosslinking of PVA by CCl_4 or trichloroethylene (TCE).

In the case to determine the number of truely grafted branches, the unreacted PVA was also extracted with water-n-propanol (75 : 25) mixture at 95°C. The alternate extraction with benzene and water-n-propanol was continued till the amount of polymer extracted decreased to a relatively low extent. Then the PVA part in the residue was completely acetylated and further extraction was repeated for homopolystyrene with hot cyclohexane and for homopoly(vinyl acetate) with hot methanol to ensure the complete isolation of the graft copolymer. The residue was re-dissolved in benzene or dioxane and precipitated into n-hexane or water. This procedure was repeated several times. The acetylation re-

duced the extraction time to a considerable extent. When no more polymer was extracted with either of the solvents, the final residue was regarded as pure graft copolymer and the percent graft was calculated by the equation (2-2).

4) Determination of molecular weights and chemical compositions.

The molecular weight of the homopolymer was estimated from the limiting viscosity number $[\eta]$ in benzene with the use of the equations,

$$[\eta] = 1.13 \times 10^{-6} \bar{M}_v^{0.73} \quad (\text{polystyrene, } 25^\circ C) \quad (4)$$

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_v^{0.76} \quad (\text{PMMA, } 30^\circ C) \quad (5)$$

Osmotic pressure measurements were carried out with a High-Speed Membrane Osmometer (Hewlett Packerd Co., 502-type) in toluene at 30°C for the mother PVA, the isolated graft copolymer and the grafted branch polymer, after the hydroxyl groups in each polymer were completely acetylated in acetic anhydride-pyridine (1 : 2) mixture. The grafted branch was separated from the backbone by cleaving 1,2-glycol bonds in the hydrolyzed graft copolymer with sodium metaperiodate in DMF. The chemical composition of the graft copolymers was determined from the alkali-consumption at the hydrolysis of the acetylated graft copolymers in benzene-methanol (20 : 1) mixture with N/4 methanolic NaOH. More detaild procedure of the characterization will be shown in Chapter 4.

RESULTS AND DISCUSSION

1) Effects of swelling agent

In the present work the grafting was carried out by using styrene and MMA as monomer, and methanol and water as swelling agent. These swelling solvents, such as methanol, are known to be very effective to promote the grafting (1) not only onto PVA(6, 7) , but also onto nylon(8 - 11), cellulose(12 - 18), poly(ethylene terephthalate)(11, 19) etc. (9, 20 - 23)

Figures 3-1 and 3-2 show the influences of methanol on the grafting of styrene and Figures 3-3, 3-4 and 3-5 on the grafting

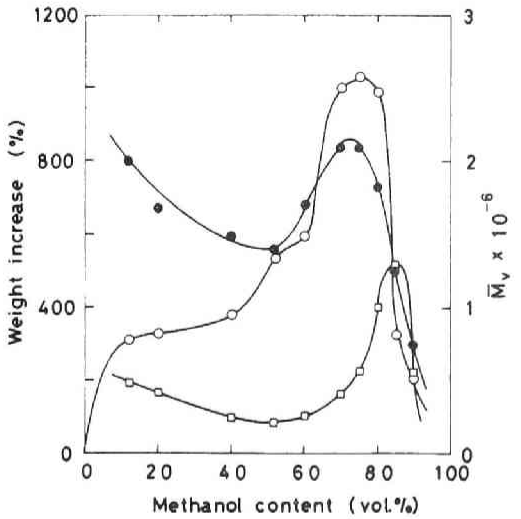


Fig. 3-1. Effects of methanol on weight increase and $\bar{M}_v$ of homopolystyrene at mutual grafting of styrene onto dry PVA films ; radiation dose = 2.5 x 10^5r, temp. = 55°C,
(●) : $\bar{M}_v$ of homoPS formed in the interior of films,
(○) : weight increase,
(□) : $\bar{M}_v$ of homoPS formed in the outer solution.

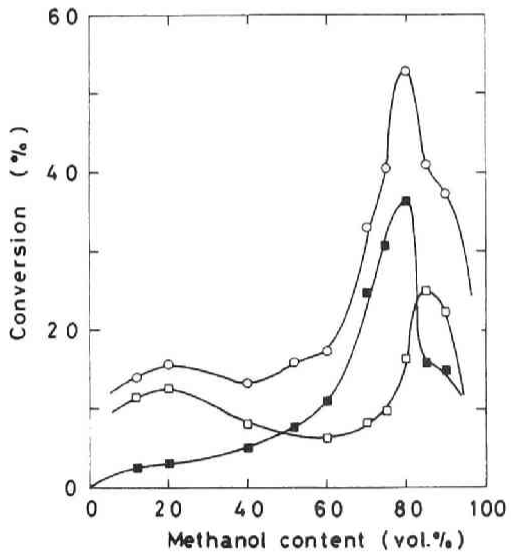


Fig. 3-2. Effects of methanol on monomer conversions at mutual grafting of styrene onto dry PVA films ; radiation dose = 2.5 x 10^5r, temp. = 55°C, (○) : total conversion, (□) : conversion in the outer solution, (■) : conversion in the interior of films.

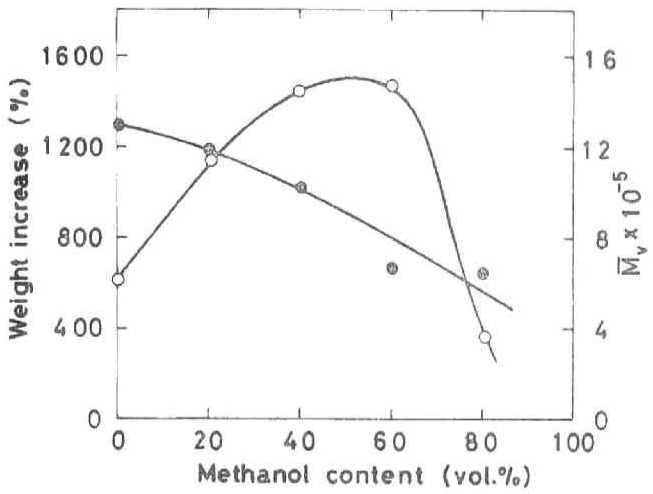


Fig. 3-3. Effects of methanol on weight increase and $\bar{M}_v$ of homo-PMMA at mutual grafting of MMA onto water-swollen PVA films (DS = 0.66) ; radiation dose = 2.4×10^5r,
(○) : weight increase,
(●) : $\bar{M}_v$ of homoPMMA formed in the interior of films.

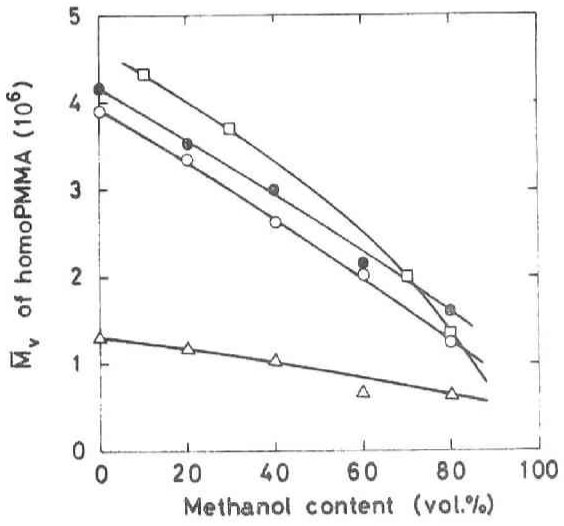


Fig. 3-4. Effect of methanol on the molecular weights of homo-PMMA's formed at mutual grafting of MMA onto water-swollen PVA films ; (□) : DS = 0, (△) : 0.66, (●) : 1.2, (○) : 2.3 .

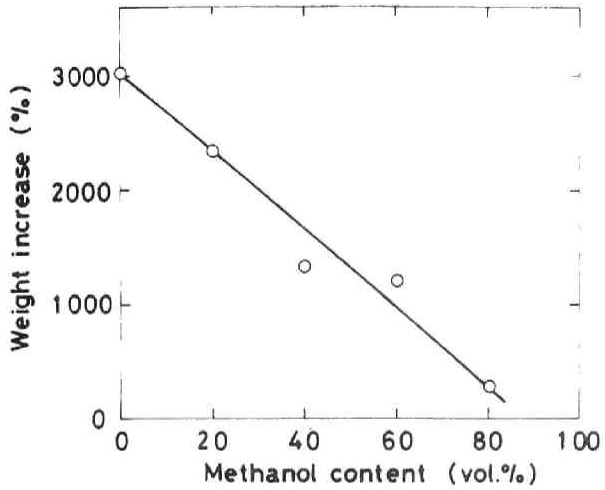


Fig. 3-5. Effect of methanol on weight increase at mutual grafting of MMA onto highly water-swollen PVA films(DS = 2.3) ; radiation dose = 9.0×10^4r, 50°C.

of MMA, respectively. The grafting of styrene was carried out by the mutual irradiation method onto dry PVA films at 55°C. The dose rate and the total dose are 6.0×10^3 r/hr and 2.5×10^5 r, respectively. The mutual grafting of MMA was carried out onto dry or water-swollen films with a dose of 9.0×10^4 r. The degree of swelling, defined as gram water contained in one gram PVA film, varied from 0 to 2.3. As can be seen, methanol actually promotes both graftings, unless the degree of water-swelling of the film is high. However, comparison of Figs. 3-1 and 3-3 reveals clearly that the variation of molecular weight as well as the weight increase with the methanol content is different between the grafting of MMA and that of styrene. This indicates that the swelling agents have several effects other than to accelerate the diffusion of monomer into the substrate matrix. Therefore, in the following we will discuss the solvent effects other than this simple penetration by classifying into some representative ones and clarify as much as possible whether the weight increase is due mainly to the increase in the number or the length of polymer chains formed.

1-1. Gel effect

The steep rise in the weight increase owing to the presence of solvent is frequently ascribed to the so-called gel effect(9, 14, 16, 18, 21, 22)(Trommsdorff effect(24)). If this effect is predominant, the molecular weight of the polymer formed should be increased in proportion to the weight increase. This case is seen just in Fig. 1, where the results of grafting of styrene in the presence of methanol were given. Several interesting trends can be seen from the results. The first is that when methanol was added to the monomer, the extent of grafting was increased first gradually, reached a maximum at methanol contents of about 60 to 80 % and then decreased rapidly. Furthermore it is seen that the methanol content where the homopolystyrene formed in the films has the maximum molecular weight agrees with the methanol content where the weight increase becomes maximum. Therefore it is obvious that the steep rise of the weight increase around the methanol content of 75 % must be principally due to the gel effect.

On the other hand, the methanol contents where the homopolymer has the maximum molecular weight are somewhat different between the homopolystyrene formed in the films and that in the outer solution of films. This may be attributed to the difference between the concentration in the films and that in the outer solution. However the difference seems not to be so significant as that in the grafting of styrene onto polyethylene(22, 23) or cellulose acetate(17). Another remarkable feature is that the molecular weight of the homopolystyrene formed in the films is about twice larger than that formed in the outer solution. This result may be explained in terms of the matrix effect due to the polymer substrate in which the mobility of polymer chains is strongly restricted. Since the gel effect is substantially originated to the decrease in the rate of collision of mutual propagating polymer chains mainly because of high viscosity of medium, the matrix effect can be regarded as a sort of the gel effect. Methanol may cause the propagating polystyrene chains to coil up, leading to the burying of the radicals, while the substrate matrix decreases the mobility of the propagating polymer chains through the gel-like property.

1-2. Diluent effect

As can be seen in Fig. 3-4, the molecular weight of PMMA homopolymer formed in PVA films is decreased steadily with increasing methanol content, in contrast with the grafting of styrene. Huang (14) also observed in rayon-styrene grafting the monotonous decrease of the molecular weight of PS branch with the increasing content of acetone, which is a non-solvent for PS.

The reason of the different influence of methanol content on molecular weight change in the MMA and styrene graftings is not clear, but it seems probable that methanol coagulates polystyrene much stronger than PMMA, giving rise to the significant gel effect in the grafting of styrene. Anyhow the above results suggest that the role of swelling agent in the heterogeneous grafting is not simple and should be discussed by taking various effects into consideration.

Two factors may be important to explain the result in Fig. 3-4 that the molecular weight of homopolymer is monotonously decreased with the methanol content. One is the dilution of monomer with methanol and the other is the radical transfer to methanol. In the mutual grafting the indirect effect due to the methanol radicals formed directly by irradiation should be further taken into consideration similarly as in the radiation-induced homopolymerization (25). As a result of the indirect effect the rate of initiation R_i becomes a complicated function of the concentration of swelling agent. However, in the case of MMA and methanol mixture R_i can be regarded as independent of the concentration to a first approximation, since the G-values for radical formation are nearly the same for MMA (G_R = 27.5) and for methanol (G_R = 24.0) (26). On the contrary, it is known (25) that the transfer of excited energy takes place between styrene and methanol, resulting in the pronounced increase in the polymerization rate with methanol. The small maximums of the conversion in the outer solution and the total conversion at a methanol content of 20 % observed in Fig. 3-2 may be explained in terms of this indirect effect. Here the conversions in the outer solution and in the interior of the films are the fractions of the monomer polymerized in each place to the initial total monomer and the total conversion is the sum of them.

If the diluent and the chain transfer effect are assumed to be the chief factors influencing the degree of polymerization of the homoPMMA, $\bar{P}$, it is given by

$$\frac{1}{\bar{P}} = C_M + C_S\frac{[S]}{[M]} + \frac{k_t^{1/2}}{k_p}\cdot\frac{R_i^{1/2}}{[M]} \qquad (3\text{-}1)$$

where [S] and [M] are the concentrations of solvent and monomer in the film, C_M and C_S the chain transfer constants to monomer and solvent, k_t and k_p the rate constants of termination and propagation, respectively. If [M] and [S] are assumed to be proportional to those of the outer solution [M'] (=k'[M]) and [S'] (= k''[S]), the following equation is obtained

$$\frac{1}{\bar{P}} = C_M - \frac{\rho_S M_{O,M}}{\rho_M M_{O,S}}\cdot\frac{k''}{k'}\cdot C_S + \left(C_S k''\cdot\frac{\rho_S M_{O,M}}{\rho_M M_{O,S}} + \frac{k_t^{1/2}R_i^{1/2}}{k_p}\cdot\frac{M_{O,M}}{\rho_M}\right)\cdot\frac{1}{k'v'} \qquad (3\text{-}2)$$

where v' is the volume fraction of the monomer in the outer monomer solution, $M_{O,M}$ and $M_{O,S}$ are the molecular weight of monomer and solvent, and ρ_M and ρ_S are the density of monomer and solvent, respectively. In this equation the concentration is expressed by mol/ml. Therefore, the value of $C_M - (\rho_S M_{O,M}/\rho_M M_{O,S})(k''/k')C_S$ can be determined as the intercept of a plot of $1/\bar{P}$ against $1/v'$. The plot is shown in Fig. 3-6, where it is seen that the intercepts are 1.0×10^{-5} regardless of the degree of swelling of the film. As C_M is 1.0×10^{-5} according to the literature (27), C_S is found to be zero. It is therefore concluded that the decrease in length of the homopolymer is attributed to the dilution effect of methanol.

Consequently the change of weight increase shown in Fig. 3-3 should be explained in terms of the penetrating effect of methanol. The monotonous decrease in the weight increase with the methanol content shown in Fig. 3-4 may be due to the higher affinity of water with PVA than of methanol, which repels water from the PVA.

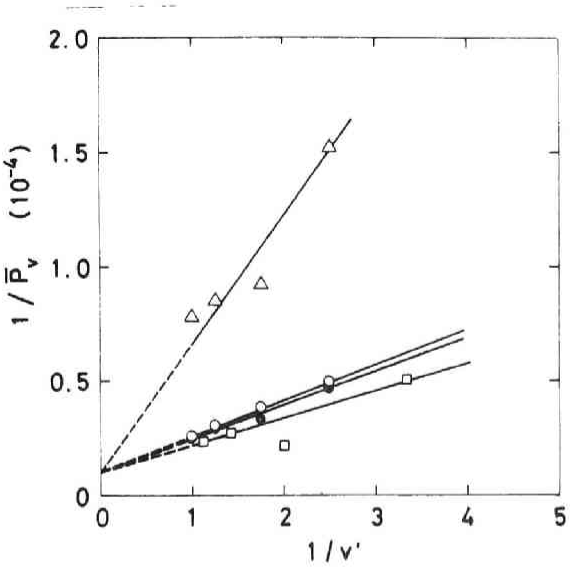


Fig. 3-6. Plots of $1/\bar{P}_v$ versus 1/v' according to eq. (3-2); (□) : DS = 0, (△) : 0.66, (●) : 1.2, (○) : 2.3 .

2) Chain transfer agent effect

As is demonstrated above and in other works(14,18,19,22,28), the length of polymer chains formed during the heterogeneous grafting is extremely long compared with that of backbone because of the matrix effect of the substrate polymer. Actually the polymer chain appears to be able to grow almost to the upper limiting length which is determined by the radical chain transfer to monomer. For this reason one can say that the radiation grafting is a model system to investigate the polymerization mechanism in a matrix or a heterogeneous medium.

One of the features of heterogeneous polymerizations is known to be the decrease in the total conversion of monomer with the increasing concentration of a chain transfer agent, even if it is not a degradative one(2,3). We found similar results also in the graftings. Fig. 3-7 shows the result of the pre-irradiation grafting of styrene onto PVA in the presence of carbon tetrachloride(CCl_4), a strong chain transfer agent for styrene. The dry PVA films were pre-irradiated to a dose of 1.0×10^6r at a dose rate of 8.4×10^4 r/hr and then grafted in styrene-methanol (40 : 60) mixture containing CCl_4. This agent did not cause any

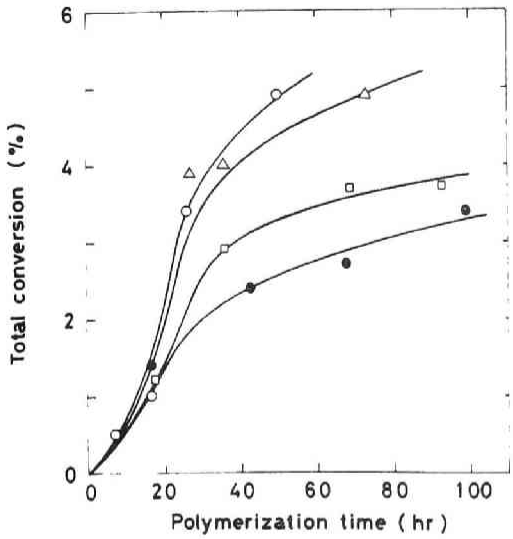


Fig. 3-7. Effect of CCl_4 on the overall rate of polymerization at pre-irradiation grafting of styrene onto dry PVA films; Methanol/Styrene = 60/40, (○) : $[CCl_4]/[St]$ = 0, (△) : 0.01, (□) : 0.05, (●) : 0.10.

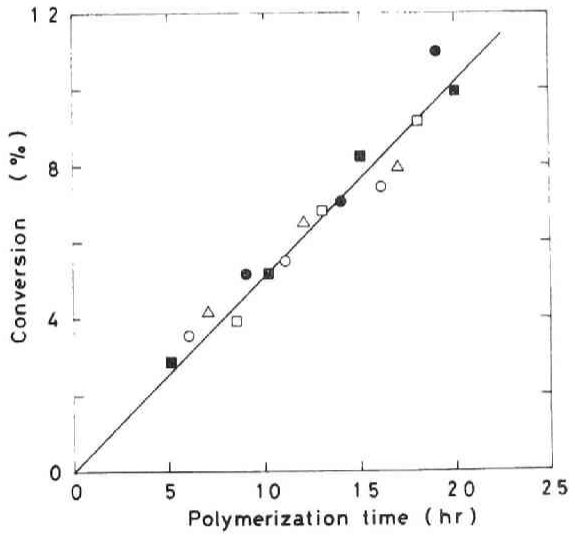


Fig. 3-8. Effect of CCl_4 on the rate of polymerization at catalytic polymerization of styrene; AIBN = 1.0 x 10^{-2} mol/l; Methanol/Styrene = 60/40; (●) $[CCl_4]/[St]$ = 0, (□) 0.025, (△) 0.050, (○) 0.075, (■) 0.10.

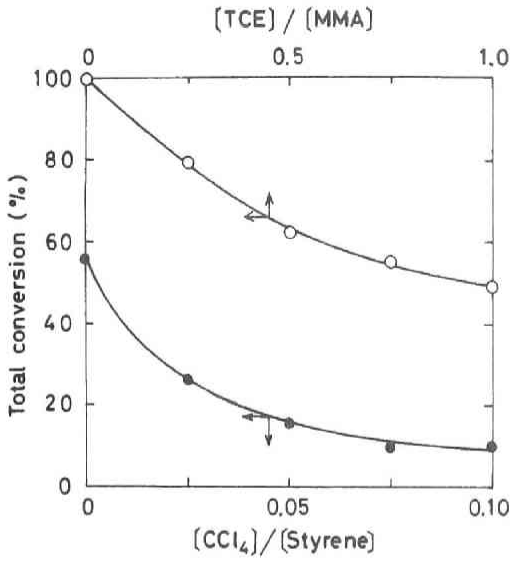


Fig. 3-9. Effect of chain transfer agents on the total conversions at the mutual graftings; 50°C ; (○) : PVA-MMA-TCE system, Methanol/MMA = 60/40, radiation dose = 9.0×10^4 r, DS of PVA films = 2.3, (●) : PVA-styrene-CCl_4 system, Methanol/Styrene = 80/20, radiation dose = 1.44×10^5 r, DS of PVA films = 0.66.

reduction of the conversion in the catalytic solution polymerization of styrene with the use of 1.0×10^{-2} mol/l AIBN, as shown in Fig. 3-8. As is seen in Fig. 3-9, the similar results were observed also in the mutual graftings of styrene and MMA, where CCl_4 and trichloroethylene(TCE) were used as chain transfer agents, respectively.

2-1. Change of the number of branches by the chain transfer agent

To study the effect of chain transfer agent on the grafting, it is important first of all to know whether the added chain transfer agent deactivates the initiating sites for grafting on the substrate polymer. For this purpose, the mutual grafting of styrene onto PVA films was carried out in the presence of a small amount of CCl_4 and the chemical structure of the graft copolymer formed was determined after complete removal of homopolystyrene and the unreacted PVA. The results are tabulated in Tables 3-1 and 3-2 together with the grafting conditions. It is seen that

Table 3-1. Mutual grafting of styrene onto water-swollen PVA films (DS = 0.66) in the presence of CCl_4

	M3S	M4S	M10S	M8S
Wt. of PVA film(g)	34.13[1)]	20.07[1)]	14.64[1)]	23.37[2)]
Styrene(ml)	234	119	120	119
Methanol(ml)	940	476	478	476
$[CCl_4]/[Styrene]$ (mole ratio)	0.13	0.05	0.025	0.05
Dose rate(r/hr)		1.0×10^4		
Dose(r)	4.6×10^5	4.6×10^5	4.7×10^5	4.7×10^5
Temp. ($^\circ$C)		50		
Total conv. of monomer(%)	69	100	89	93
Wt. of graft copolymer(g)	2.976	3.523	3.323	2.124
Wt. frac. of styrene part	0.533	0.635	0.676	0.677
True grafting efficiency(%)	1.1	2.2	2.0	1.5
True percent graft(%)	4.6	11.1	15.3	6.2
Frac. of reacted PVA(%)	4.1	6.4	7.3	2.9
G-value for branch formation	1.0	1.3	1.2	1.0

1) $\bar{M}_n = 5.89 \times 10^4$

2) $\bar{M}_n = 3.40 \times 10^4$

the G-values for branch formation, defined as the number of branches formed per 100 eV radiation energy, do not scatter virtually from the average value of 1.0 in the range of $[CCl_4]/[monomer]$ from 0.025 to 0.13. This important conclusion that the chain

Table 3-2. Chemical structures of PVA-styrene graft copolymers

Sample	VAC cont. of acetylated graft copolymer (wt%)	$\bar{M}_n \times 10^{-5}$				Numbers in a graft copolymer molecule	
		Acetylated graft copolymer	Backbone PVAC [1]	Branch PS [1]	Isolated branch	Backbone [2]	Branch
M3S	63.1	3.54	2.23	1.31	1.04	1.94	1.26
M4S	53.0	3.90	2.07	1.83	1.88	1.80	0.97
M9S [3]	58.9	4.02	2.36	1.66	1.40	2.05	1.18
M10S	48.4	6.03	2.92	3.11	2.71	2.54	1.15
M8S	48.2	2.89	1.39	1.50	1.41	2.09	1.06

1) Calculated by values of the composition and $\bar{M}_n$ of the acetylated graft copolymer.
2) ($\bar{M}_n$ of backbone PVAC) / ($\bar{M}_n$ of mother PVAC)
3) Prepared under the same condition as sample M4S.

transfer agent does not affect the branch number is also supported from the fact that the fraction of grafted PVA which is directly related to the number of branch formed except for M8S remains roughly constant regardless of the variation of CCl_4 concentration. On the contrary, Hayakawa et al.(29) and Huang(14) reported that the number of branch increased with addition of CCl_4 in the graftings of styrene onto cellulose acetate and rayon, respectively. However it is questionable in these cases whether the homoPS formed within the fibers was completely removed.

2-2. Chain transfer constant in the grafting

In Fig. 3-10, $1/\bar{P}$ was plotted against the initial concentration ratio of CCl_4 to styrene to estimate the chain transfer constant C_S. The C_S values calculated from slopes of the linear curves in Fig. 3-10 are 6.0×10^{-3} for mutual irradiation grafting, 7.5×10^{-3} for pre-irradiation grafting and 6.7×10^{-3} for the conventional polymerization with AIBN. Also in the graftings of MMA onto PVA (30) and styrene onto cellulose acetate(29), the

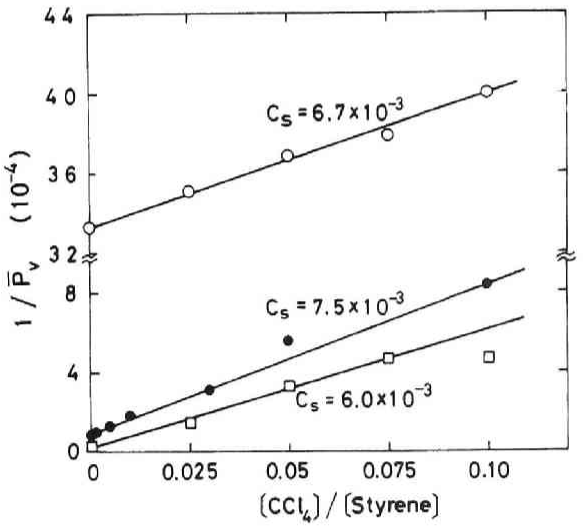


Fig. 3-10. Effect of CCl_4 on the DP's of homopolystyrene formed at various polymerizations ; (○) : catalytic polymerization (AIBN = 1.0×10^{-2} mol/l), (●) : pre-irradiation grafting, (□) : mutual grafting.

two values of C_S obtained from the grafting and catalytic polymerization were in good agreement. These results do not seem unreasonable, since the concentration ratio of chain transfer agent to monomer in the vicinity of the growing chain ends in the film would be nearly equal to that for the growing chains at the conventional polymerization and in addition the rate constants of polymerization (k_p) and of chain transfer (k_{tr}) may be same in the grafting and the catalytic polymerization.

2-3. Decrease in the total conversion

The above experiments denote that the chain transfer agent neither deactivates the primary radicals on the substrate polymers, nor behaves abnormally, at least, with respect to the change of polymer chain length. However, it decreases greatly not only the percent graft(31), but also the total conversion of monomer, as shown in Figs. 3-7 and 3-9. To gain a deep insight on the mechanism, we determined the weight of homopolymer formed in the film and in

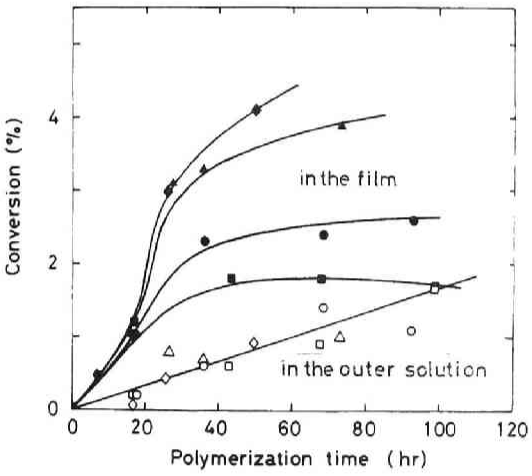


Fig. 3-11. Effect of CCl_4 on the monomer conversions in the film and in the outer solution at pre-irradiation grafting of styrene onto PVA films (Methanol / Styrene = 60 / 40). (◇, ◆) $[CCl_4]/[\text{styrene}]$ = 0, (△, ▲) 0.01, (○, ●) 0.05, (□, ■) 0.10.

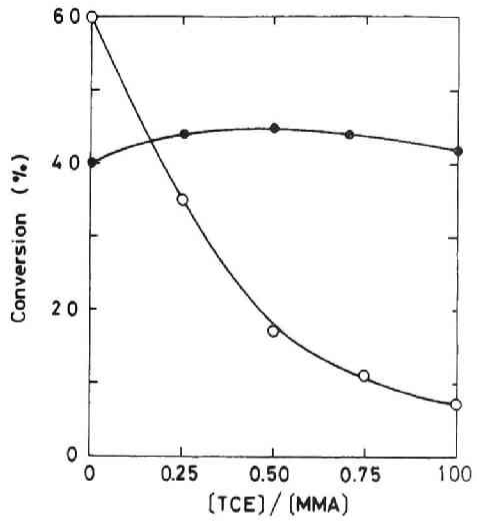


Fig. 3-12. Effect of TCE on the monomer conversions in the PVA films and in the outer solution at mutual grafting of MMA onto PVA films (Methanol/MMA = 60/40); (○) in film, (●) in outer solution.

Table 3-3. Effect of CCl_4 on the mutual grafting of styrene onto water-swollen PVA films (DS=0.66), methanol/styrene = 80/20, radiation dose = 1.44×10^5 r, 50°C.

	S75	S76	S77	S78	S79
$[CCl_4]/$(styrene) (mole ratio)	0	0.025	0.050	0.075	0.10
Conv. in the outer soln. (%)	14.6	15.1	11.2	7.3	8.0
Conv. in the PVA films (%)	40.8	7.7	4.5	2.5	2.0
Total conversion (%)	55.4	22.8	15.7	9.8	10.0
$\bar{M}_v$ of homoPS (10^5)	51.0	7.07	3.12	2.24	2.24
Number of PS molecules formed in PVA films (10^{17})	1.05	1.42	1.86	1.42	1.17

the outer solution as well as the molecular weight of both polymers. The yield of homopolymer, expressed here as conversion, was given in Figs. 3-11 and 3-12 and Table 3-3. It is seen that the weight of polymer formed in the film is decreased with the concentration of chain transfer agent, whereas the conversion in the outer solution does not depend actually on the concentration for those cases. The influence of CCl_4 through the indirect effect on the the mutual grafting can be neglected, because the decrease in the polymer yield is observed also in the pre-irradiation grafting. It is interesting to point out that, as is seen in Table 3-3, the number of polymer formed in the film remains constant regardless of the CCl_4 concentration within the experimental error. It follows that the CCl_4 radicals produced as a result of radical transfer from the growing chain disappear rapidly from the substrate matrix. Judging from the fact that the yield of homopolymer in the outer solution is constant or rather decreased with the CCl_4 concentration, it seems to be probable that the radicals from CCl_4 disappear in the film as a result of the recombination.

CONCLUSION

1) The presence of methanol in the monomer enhances the diffusion of monomer into the substrate film, resulting in increase of the number of polymer chains.
2) The monomer diffusion into the film is more largely enhanced by water, which pre-swells the film, than methanol whose affinity for PVA is much lower than water.
3) In the grafting with styrene, methanol gives rise to the gel effect to a considerable extent in the content range near 75 %. As a result the length of polymer chains becomes very long and hence the percent graft is increased in proportion to the chain length.
4) In contrast with the grafting with styrene, methanol in the grafting with MMA dose not cause any gel effect, but acts merely as a simple diluent. The chain length is decreased with the methanol content as obeying the normal polymerization kinetics.
5) The percent graft as well as the total conversion are decreased

significantly when the graftings of styrene and MMA are carried out in the presence of CCl_4 and TCE, respectively, though they are found not to be degradative chain transfer agents in the conventional, catalytic polymerizations. This may be a reflection of the heterogeneous polymerization process by which the graftings proceed.

6) The chain transfer constant of CCl_4 calculated from the variation of molecular weight of the homopolystyrene formed in the film is in good agreement with that found in the conventional polymerization of styrene in the presence of CCl_4.

7) The characterization of the graft copolymers freed from the homopolymers proves that the number of truely grafted branches produced per unit dose is not increased nor decreased by the presence of CCl_4.

REFERENCES

1) H. A. J. Battaerd and G. W. Tregear, Graft Copolymers, Interscience, New York, 1967.
2) C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, The Kinetics of Vinyl Polymerization by Radical Mechanisms, Butterworths, London, 1958.
3) J. C. Bevington, Radical Polymerization, Academic Press, London and New York, 1961, p.130.
4) C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, Trans. Faraday Soc., 46, 1107 (1950).
5) T. G. Fox, T. B. Kinsinger, H. F. Mason, and E. M. Schuele, Polymer [London], 3, 71 (1962).
6) I. Sakurada, T. Okada, and E. Kugo, Isotopes and Radiation, 2, 296, 306, 316, 581 (1959), 3, 316, 329, 379, 406 (1960); 4, 240 (1961).
7) A. Chapiro and V. Stannett, Int. J. Appl. Rad. and Isot., 8, 164 (1960).
8) A. Országh and J. Zurakowska-Országh, Ind. Uses of Large Radiation Sources, 1, 301 (1963).
9) G. Odian, T. Acker, and M. Sobel, J. Appl. Polymer Sci., 7, 245 (1963).

10) G. Odian, M. Sobel, A. Rossi, R. Klein, and T. Acker, J. Polymer Sci., A1, 639 (1963).
11) D. S. Ballantine and A. Glines, Proceedings of the 5th Conference on Radioisotopes, 2-72 (1963), Tokyo [Japan].
12) I. Sakurada, T. Okada, and S. Hatakeyama, Hōshasen Kōbunshi Kyōkai Nenpō, 2, 55 (1960).
13) S. Dilli and J. L. Garnett, J. Appl. Polymer Sci., 11, 839, 859 (1967).
14) R. Y. -M. Huang, J. Appl. Polymer Sci., 10, 325 (1966).
15) J. C. Arthur, Jr. and F. A. Blouin, J. Appl. Polymer Sci., 8, 2813 (1964).
16) Y. Nakamura, O. Hinojosa, and J. C. Arthur, Jr., J. Appl. Polymer Sci., 14, 789 (1970).
17) T. Yasukawa, Y. Sasaki, and K. Murakami, Makromol. Chem., 153, 323 (1972).
18) H. Sobue, K. Matsuzaki, H. Komagata, and A. Ishida, J. Polymer Sci., C 2, 415 (1963).
19) Y. Ikada, T. Kawahara, and I. Sakurada, presented at the 18th Polymer Symposia of Soc. Polymer Sci. Japan, 1969, Preprint, p.243.
20) J. Dobó, M. Somogyi, and L. Kiss, Large Radiation Sources in Industry, Vol. I, International Atomic Energy Agency, Vienna, 1960, p.423.
21) G. Odian, A. Rossi, and E. N. Trachtenberg, J. Polymer Sci., 42, 575 (1960).
22) G. Odian, M. Sobel, A. Rossi, and R. Klein, J. Polymer Sci., 55, 663 (1961).
23) S. Machi, I. Kamel, and J. Silverman, J. Polymer Sci., A-1, 8, 3329 (1970).
24) E. Trommsdorff, H. Kohle, and P. Lagally, Makromol. Chem., 1, 169 (1948).
25) A. Chapiro, Radiation Chemistry of Polymeric Systems, Interscience, New York, 1962, p.285.
26) A. Prevot-Bérnas, A. Chapiro, C. Courin, Y. Landler, and M. Magat, Disc. Faraday Soc., 12, 98 (1952).
27) Polymer Handbook, Ed. by J. Brandrup and E. H. Inmmergut, Interscience, 1966.

28) I. Sakurada, S. Matuzawa, and Y. Kubota, Makromol. Chem., 69, 115 (1963).
29) K. Hayakawa, K. Kawase, and T. Matsuda, Chem. High Polymer [Japan], 20, 609 (1963).
30) I. Sakurada, Y. Ikada, and T. Yamaoka, Bull. Inst. Chem. Res., Kyoto Univ., 45, 1 (1967).
31) A. J. Restaino and W. N. Reed, J. Polymer Sci., 36, 499 (1959).

CHAPTER 4

CHEMICAL STRUCTURE OF POLY(VINYL ALCOHOL)-METHYL METHACRYLATE GRAFT COPOLYMERS PREPARED BY VARIOUS METHODS

INTRODUCTION

Within recent years a great number of investigations(1) have been carried out on the grafting. These works are mainly concerned with methods, kinetics or mechanisms of the grafting. On the other hand, very little effort has been devoted to the characterization of graft copolymers produced (2-14). However, it is essential to elucidate the chemical structure of graft copolymers, not only to learn the grafting mechanism, but also to evaluate properties of the graft copolymers. In our laboratory extensive studies have been done on the radiation-induced graft copolymerization of vinyl monomers onto poly(vinyl alcohol) (PVA) (15). Concerning the chemical structure of graft copolymers, it was pointed out ten years ago(16) that graft copolymers of methyl methacrylate (MMA) on PVA prepared by an ordinary irradiation technique consisted of one mother PVA molecule (DP about 1,000) and one long poly(methyl methacrylate) (PMMA) branch (DP about 30,000). We have then begun with experiments to prepare graft copolymers whose backbone and branch have practically the same length(17,18). In that case graft copolymers were prepared by pre-irradiation technique as before, but monomer solution was different from that used in the previous experiments ; trichloroethylene (TCE), a chain transfer agent, was added to the solution to shorten the length of the branches. The number of branches of the copolymers thus obtained was in all cases one, but unexpectedly the number of mother PVA molecules in a graft copolymer ranged from 0.9 to 5.7.

The reason why the backbone of these graft copolymers consisted of several mother PVA molecules was made clear recently (19). It was observed that unirradiated pure PVA films were slightly colored yellowish when heated in a methanol/TCE (1 : 1) mixture at the temperature of extraction of homoPMMA (80°C). The colored films were partially insoluble in boiling water, indicating that

crosslinking took place between PVA molecules due to TCE. On the contrary, neither coloration nor insolubilization was observed for the films treated in methanol-TCE at temperatures lower than 50°C. The graft films prepared in the presence of TCE were colorless, but became colored after continuous extraction with boiling benzene for one week without exchanging the benzene, and were no more soluble in dimethyl sulfoxide (DMSO), a solvent of both PVA backbone and PMMA branch. However, when the graft films were at first immersed in water or extracted with boiling water prior to the extraction with boiling benzene, they were soluble in DMSO and not colored at all. Therefore it is expected that a graft copolymer with the backbone consisting of one mother PVA can be obtained, if the extraction is carried out at first with water. Preliminary experiments have verified the expectation.

The main purpose of this chapter is to clarify the chemical structure of PVA graft copolymers prepared by several different methods, and to obtain well-characterized graft copolymer samples for the studies of their properties. The methods employed in the present study are both radiation and chemical ones. The techniques used for the radiation-induced grafting are pre-irradiation and mutual irradiation with gamma-rays from ^{60}Co. The chemical grafting was carried out by the use of potassium persulfate(KPS) as an initiator (initiator method). In addition, grafting was tried under conditions that neither irradiation nor initiator was used (method of IMOTO (20, 21)) . In all cases MMA was grafted onto films of PVA in the presence of TCE.

EXPERIMENTAL

1) Films

Aqueous solution of purified PVA was cast on glass plates at room temperature. The films formed were cut into strips of 5 x 1 cm, and dried under vacuum for 2 days at 50°C. The thickness of films was 0.1 mm except those used for pre-irradiation grafting which had a thickness of 0.05 mm. For the grafting by mutual irradiation (MIM) and KPS initiator, films were prepared from fractionated PVA, whereas unfractionated PVA was used in other cases.

2) Pre-swelling of films

In order to proceed with the grafting reaction as homogeneously as possible throughout the whole films, they were treated with swelling agents such as water or water-methanol prior to grafting except for the case of pre-irradiation method. Table 4-1 lists the swelling conditions and the observed degrees of swelling.

Table 4-1. Pre-swelling of PVA-films

Grafting method	Swelling			Degree of swelling[a] (g/g)
	Agent	Temp. (°C)	Time	
Mutual irradiation	H_2O/MeOH(40:60)	50	24 hrs	1.64
Pre-irradiation	—	-	—	—
KPS	1.25 % aqu.soln. of KPS	20	3 min	2.74
Without initiator	water	20	3 min	2.69

a) $\frac{\text{weight increase after swelling}}{\text{weight of dry films}}$

In the case of grafting by KPS, films were swollen with an aqueous solution of the initiator to impregnate the films with KPS. In the pre-irradiation grafting the pre-swelling was not performed, and the dry films were submitted to the grafting reaction immediately after the irradiation.

3) Graft copolymerization

A pre-swollen or pre-irradiated film was put into a reaction tube and monomer solution containing TCE and methanol, whose contents are shown in Table 4-2, was added to it. They thoroughly degassed by conventional freezing and thawing cycles.

Table 4-2. Composition of monomer solution for the grafting

Grafting method	MeOH / MMA (vol.ratio)	[TCE]/[MMA] (mole ratio)	Solution/Film (ml/g)
Mutual irradiation	80/20	0.5	46.6
Pre-irradiation	60/40	0.5	20.2
KPS	0/100	1.5	51.2
Without initiator	60/40	0.5	27.2

The amount of TCE was fixed on the basis of results of our previous experiments (17) so as to make the branch length comparable with that of the backbone. In the pre-irradiation grafting, the irradiation was carried out at room temperature in the presence of air to a desired dose. The dose selected was the optimum dose, above which the PVA was degraded to a significant extent (22), and below which the yield of grafting was too low. The pre-irradiated films and the monomer solution were separately degassed by the use of a breakable seal, and then allowed to contact with each other after the tube was sealed. After the sealed tubes were preserved overnight in a refrigerator in each case, grafting

Table 4-3. Conditions of grafting reactions

Grafting method	Temp. (°C)	Dose rate (r/h)	Dose (r)	KPS (mole%) b)	Polym. time(h)
Mutual irradiation	50	6.1×10^{3}	3.0×10^{5}	—	49
Pre-irradiation	50	6.6×10^{4} a)	1.0×10^{6} a)	—	99
KPS	60	—	—	0.57	5
Without initiator	60	—	—	—	150

a) Dose rate and dose of pre-irradiation.

b) Mole% to the basic molecule of PVA.

reaction was conducted by rotating the tubes incessantly in a water bath kept at a given temperature. The detailed grafting conditions are tabulated in Table 4-3.

4) Isolation of graft copolymer

After separation of the graft films from homoPMMA formed in the outer solution, isolation of pure graft copolymers from both the homoPMMA and the unreacted PVA existing in the crude graft films was effected by alternate repetition of extraction. The unreacted PVA was extracted with water or water-n-propanol (75 : 25) mixture and the homoPMMA with benzene mainly at their boiling temperatures. In every case the extraction was started with water, as noted above. The cycle of extraction was continued, until the amount of extracted polymers was decreased to a negligible extent, and the residue was regarded to be the pure graft copolymer.

5) Separation of branch, acetylation, and hydrolysis

The isolated graft copolymers were divided into two parts. For the separation of the graft branch from the backbone, one of them was dissolved in DMSO which contained a small amount of periodic acid, and treated at 30°C for five hr. It is well known that ordinary PVA contains 1 - 2 mole% of 1,2-glycol linkage, which is selectively attacked and broken by periodic acid. Since the separated branch which was recovered from the DMSO solution, carries a short fragment of PVA at the end of the molecule, it was subjected to osmometry for the molecular weight determination, after acetylation of the fragment. The outline of the separation procedure is shown in Fig. 4-1.

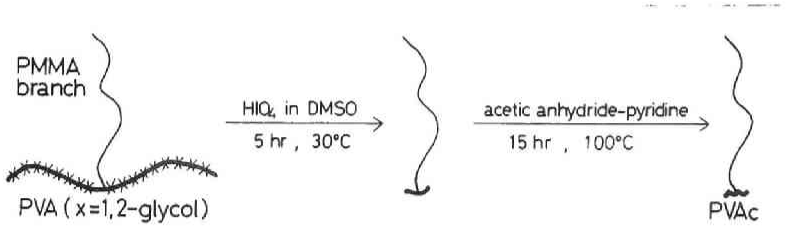


Fig. 4-1. Separation of graft branch (the content of 1,2-glycol in the PVA = 1.5 mole%)

The other part was used to convert the poly(vinyl alcohol-g-methyl methacrylate) to poly(vinyl acetate-g-methyl methacrylate) which is soluble in many conventional solvents. It should be pointed out that PVAc and PMMA are compatible in benzene over the whole polymer concentration range. The complete acetylation of hydroxyl groups in the graft copolymer and the isolated branch was effected with acetic anhydride-pyridine mixture for 15 hrs at 100°C under nitrogen.

6) Determination of composition of graft copolymers

The MMA or VAc content of the graft copolymers was calculated from the alkali-consumption by the alkaline hydrolysis of the acetylated graft copolymer under such conditions(23) that exclusively the acetylated backbone (not PMMA branch) is attacked on hydrolysis.

The details of cleaving reaction, acetylation and hydrolysis were described elsewhere(16).

7) Determination of molecular weights

Number-average molecular weights of the acetylated graft copolymers and separated branches were determined by osmotic pressure measurement in benzene at 30°C. Molecular weights of acetylated mother PVA and homoPMMA formed in the films during the grafting were also measured by osmometry under the same condition as that for the graft copolymer. The polymers to be measured were purified by precipitation into petroleum ether from the filtered benzene solution and then dried at 50°C under reduced pressure. These polymers were dissolved in benzene and their osmotic pressures were measured with the aid of a "502 High-Speed Membrane Osmometer" manufactured by Mechrolab Inc., and a "CMS-1 Recording Osmometer" by Melabs. The results obtained by the two different osmometers were in good agreement with each other. The membranes used were "Ultracella-Filter(feinst)" of Sartorius Membranfilter GmbH.

RESULTS AND DISCUSSION

1) Extraction of homopolymers

Regardless of the grafting methods employed, the removal of the homopolymers by alternate extraction was not carried out so simply as in the cases described in Chapter 2, because the molecular weight of PMMA was decreased with a chain transfer agent so as to be comparable with that of the backbone. We presented here merely the results obtained at the mutual grafting as a typical example. In Tables 4-4 and 4-5 are shown the results.

Table 4-4. Extraction of homoPMMA with benzene at 80°C (mutual grafting)

Step of extraction procedure	Time (days)	Extracts (g)	Step of extraction procedure	Time (days)	Extracts (g)
2nd	4	32.43[a)]	6th	2	0.05
4th	3	0.19	8th	3	0.02

a) Number-average degree of polymerization, $\bar{P}_n$ = 1,770.

The extraction of homoPMMA with benzene was rather simple, and the extracts were confirmed from infra-red spectroscopy to be pure homoPMMA at each step of the extraction. In the case of extraction of the unreacted PVA, however, the circumstances were much complicated, as may be seen from Table 4-5. For instance, when a water/n-propanol(75 : 25) mixture, which is known as a better solvent for PVA than water (24), was used instead of water at the third step of the extraction, the extract solution became completely milky and the separation of the two phases was not successful even by centrifugation at 3,000 rpm for 1 hr. In that case, therefore, the turbid solution was concentrated under vacuum below 50°C to dryness, and the recovered residue was submitted to further extraction under a milder condition, that is, with pure

Table 4-5. Extraction of unreacted PVA[a] (mutual grafting)

Step of extraction procedure	Solvent	Temp. (°C)	Time	Extracts (g)	Appearance of solution
1st	Water	80	1 hr	0.544	clear
	Water/n-propanol	80	1 day	2.86[b]	clear
3rd	Water/n-propanol	80	1 hr	—	milky
5th	Water	80	3 days	3.35	clear
	Water	100	3 days	0.67	clear
7th	Water	80	2 days	0.021	slightly turbid
	Water/n-propanol	80	4 days	0.419	slightly turbid
	Water/n-propanol	100	2 days	0.131	turbid
9th	Water/n-propanol	100	2 days	trace	turbid

a) The weight of starting PVA = 10.73 g, and $\overline{P}_n$ = 2,140.
b) $\overline{P}_n$ = 1,860.

water at 80°C. Then the extract solution became practically clear and could readily be separated from the residue. When it became difficult to separate the extract solution from the residue by simple decantation or filtration procedures, the separation was carried out by centrifugation. As demonstrated above, the extraction of the unreacted PVA was considerably troublesome. However, in our case, the homoPMMA and unreacted PVA could be removed satisfactorily from the graft copolymer by a suitable choice of extraction conditions.

In extraction from graft films prepared by the pre-irradiation technique, the films were dissolved in DMSO at the middle step of extraction, and re-precipitated into methanol to alter the state of mixing of PVA and PMMA. Further alternate extrac-

tion was continued for this pulverized product. The films before dissolution in DMSO appeared like a hollow beanpod, evidently indicating that the grafting reaction was confined to the surface regions of the films. A similar result was also reported by Campbell et al.(25) In other cases dissolution in DMSO was not necessary, because the films were broken to pieces gradually during the extraction. In the case of mutual irradiation also the grafting did not proceed throughout the whole film, when it was not sufficiently pre-swollen.

As mentioned above, the separation of the grafting product into its three possible constituents by extraction method is very time-consuming, whereas that of a mechanical mixture into the constituents is usually easy. This suggests that the graft copolymer strongly affects the extractability of the homopolymers. Some problems on the isolation of pure graft copolymer will be discussed in Chapter 6.

2) Results of graft copolymerizations

The results of graft copolymerizations are summarized in Table 4-6. When the homoPMMA was removed not so vigorously as by the repetition of alternate extraction, but only by the simple extraction with benzene as usually done, considerably higher percent grafts were obtained as demonstrated in Chapter 2.

We believe that the fraction of grafted PVA indicates most distinctly the characteristics of grafting methods. It is easily understandable that the fraction of grafted PVA is remarkably low in the case of grafting without initiator. The heterogeneous distribution of graft copolymer in the case of pre-irradiation grafting may be ascribed to insufficient diffusion of the monomer into the dry films, which leads to the restricted localization of graft copolymer and the relatively low fraction of grafted PVA. The graftings by mutual irradiation and catalytic initiation with KPS, where swollen films were used, resulted expectedly in high fractions of grafted PVA.

It is noteworthy that the mutual irradiation gives lower fraction of grafted PVA than the initiation by KPS, although the total

Table 4-6. Comparison of various graftings of MMA onto PVA films

	Mutual irradiation	Pre-irradiation	KPS	Without initiator
Initiation	3.0×10^5 r	1.0×10^6 r	$\frac{[KPS]}{[VA]} = \frac{5.7}{1,000}\left(\frac{\text{mole}}{\text{ratio}}\right)$	0
Polym. time (h)	49	99	5	150
Total conversion (%)	100	18.4	21.2	14.8
Percent graft (%)	18.9	13.1	42.8	1.9
Graft efficiency (%)	2.3	10.2	6.1	1.8
Fract. of grafted PVA (%)	10.9	4.25	21.9	0.46
Location of grafting	Homo-geneous	Near the film surface	Homogeneous	Homo-geneous

conversion of monomer reached 100 % in the former case. The highest fraction of grafted PVA for the initiation by KPS may be explained mainly from the following two reasons. In the first place, the concentration of KPS could be increased to a fairly high degree without causing any appreciable side reactions such as degradation and crosslinking. Secondly, KPS and PVA form a redox system, from which radicals are produced directly on the main chains of PVA (27). However, it should be pointed out that the fraction of grafted PVA is even in this case rather too low if we recall that the amount of KPS was as high as 0.57 mole per 100 basic moles of PVA (Table 4-3). Provided that each branch is produced by one molecule of KPS, only 1.4 % of KPS is regarded to have contributed to the grafting. According to our earlier study (27) it appears that some of the KPS molecules are consumed to produce ketone groups on the main chain of PVA. The use of ceric ion, a well-known initiator of "grafting", was avoided in the present chemical grafting due to the reason that it causes exclusively main chain scission of PVA as a result of the selective reaction with 1.2-glycol linkages in PVA (28).

Considerably low graft efficiencies found in every case are due to the presence of chain transfer agent. It is a reasonable result that the graft efficiency is highest in the case of preirradiation grafting. When grafting was carried out in the absence of chain transfer agent, the graft efficiency was higher and the percent graft increased remarkably, regardless of the presence of swelling agent and the grafting methods adopted, since the branch chains grew about several tens times as long as those obtained in the present case (17, 26). It is, of course, too difficult to characterize the graft copolymers with such long branches, and in addition the graft copolymer with such an unbalanced structure is not suitable as a sample for studies of various properties of graft copolymer. The use of a chain transfer agent is favorable also due to another reason that they exclude possible termination reaction by mutual combination of growing branches, which would otherwise lead to formation of graft copolymers of the "H" type structure.

3) Molecular weights of various polymers

Typical results of osmotic presure measurements are given in Fig. 4-2. This is an example for polymers obtained at the mutual grafting.

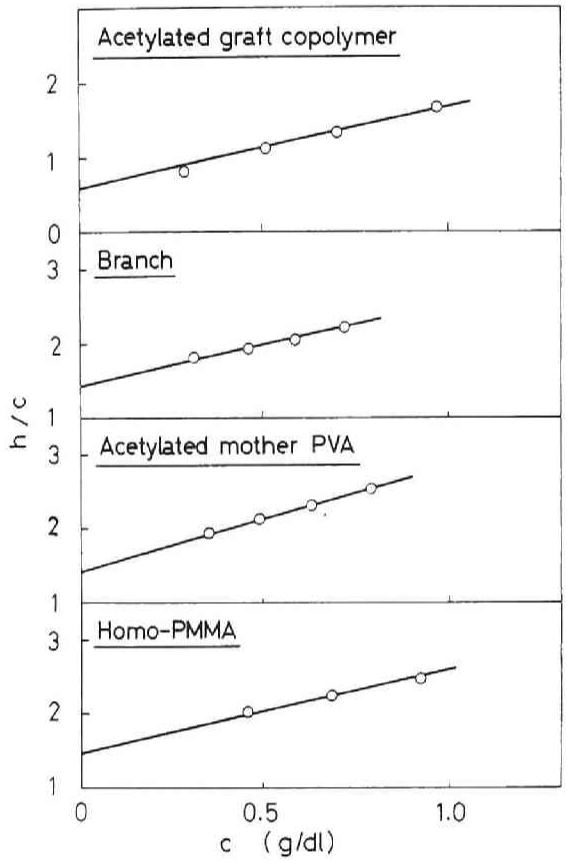


Fig. 4-2. Reduced osmotic pressures of various polymers in benzene at 30°C (mutual grafting)

The homoPMMA is the one that was formed in the films and removed at the second step of extraction (see Table 4-4). In other cases, excellent linear relationships similar to those in Fig. 4-2 were observed between the reduced osmotic pressure and polymer concentration. Table 4-7 lists the molecular weights, $\overline{M}_n$, of various polymers obtained at the different graftings, together with the chemical compositions of graft copolymers. Although the separated branch has PVAC fragment on one end of the branch chain, its additional effect was not taken into consideration for the calcu-

Table 4-7. Molecular weights and chemical compositions of graft copolymers prepared by various methods

Grafting method	$\bar{M}_n \times 10^{-5}$ Acetylated graft copolymer	Separated branch	Acetylated mother PVA	Homo-PMMA	MMA content of acetylated graft copolymer (mole %)	(wt. %)
Mutual irradiation	4.17	1.81	1.84	1.77	43.4	47.2
Pre-irradiation	6.65	4.42	1.15	4.63	57.8	61.4
KPS	3.69	1.46	1.99	1.67	36.8	40.4
Without initiator	6.88	5.32	1.15	—	65.5	68.8

lation of molecular weight of branch, because the molecular weight of the PVAc fragment was negligibly low, compared to that of the branch. It is interesting to note that the molecular weight of homoPMMA formed in the matrix of PVA films is approximately equal to that of the branch polymer. The identical finding was also observed in the previous works (18, 29).

4) Chemical structure of graft copolymers

Basing on the values given in Table 4-7 it is now possible to make clear the chemical structure of the graft copolymers without any assumption. The number of branches and mother PVA molecules in one graft copolymer molecule is calculated in the following manner. When we multiply the molecular weight of graft copolymer by the fraction of PMMA or PVAc, we get the molecular weight of PMMA or PVAc part, respectively. Dividing the molecular weight of PMMA or PVAc part by the molecular weight of separated branch or acetylated mother PVA, respectively, we

get finally the numbers of branches and mother PVA molecules of which one graft copolymer consists.

Number of branches

$$= \frac{\bar{M}_n \text{ of PMMA part in acetylated graft copolymer}}{\bar{M}_n \text{ of separated branch}}$$

$$= \frac{(\bar{M}_n \text{ of graft copolymer}) \times \begin{pmatrix}\text{wt. fraction of PMMA part} \\ \text{of graft copolymer}\end{pmatrix}}{\bar{M}_n \text{ of separated branch}} \qquad (4\text{-}1)$$

Number of mother PVA molecules

$$= \frac{\bar{M}_n \text{ of PVAc part in acetylated graft copolymer}}{\bar{M}_n \text{ of acetylated mother PVA}}$$

$$= \frac{(\bar{M}_n \text{ of graft copolymer}) \times \begin{pmatrix}\text{wt. fraction of PVAc part} \\ \text{of graft copolymer}\end{pmatrix}}{\bar{M}_n \text{ of acetylated mother PVA}} \qquad (4\text{-}2)$$

The numbers calculated in this way are given in Table 4-8, where it can be seen clearly that in every case the number of branches is about unity on the average. On the other hand, the number of mother PVA molecules is more than unity in every case; close to unity in the samples (M1M and KPS) prepared from the fractionated PVA's and to 2 in the others prepared from the unfractionated. This fact is not due to the crosslinking between mother PVA molecules as pointed above. The most reasonable reason is that mother PVA molecules with higher molecular weights are prone to be grafted more frequently. As will be shown theoretically in Chapter 5, the ratio of molecular weight of PVA part of the graft copolymer to that of the mother PVA should range from two to one in various fractions of grafted PVA, if the molecular weight distribution of the mother PVA sample is random. Thus it is proved

Table 4-8. Number of branches and mother PVA molecules in one molecule of graft copolymer

Grafting method	Number of branches	Number of mother PVA molecules
Mutual irradiation	1.09	1.20
Pre-irradiation	0.93	2.23
KPS	1.02	1.10
Without initiator	0.89	1.87

definitely that the graft copolymer consisting of one mother PVA molecule and one branch is produced irrespective of the method adopted. This fact confirms evidently that the first extraction with water prevents the formation of crosslinking between mother PVA molecules as expected above, and, besides, that the acetylated graft copolymer is dissolved monomolecularly in benzene. It should be also noted that no appreciable degradation of main chain of mother PVA occurred during the course of grafting and extraction.

If we take into account the rather low concentration of active sites for grafting produced by irradiation or KPS initiation, it seems quite reasonable that the fraction of grafted PVA and the number of branches are small. According to our statistical calculation in Chapter 5, the average number of graft branches in one graft copolymer is as low as 1.1 when the fraction of PVA subjected to the grafting is 0.20. The number increases to two, if the fraction increases to 0.75.

5) Comparison of various grafting methods

In general it is not easy to compare the results obtained by various methods, because the grafting conditions are different. In the present case, nevertheless, the comparison is possible to

a certain extent, since we selected reaction conditions under employment of TCE as a transfer agent, to make the percent graft as high as possible in each case and the grafting was always carried out in heterogeneous system to films.

Table 4-8 shows conclusively that all the grafting methods employed in the present study produce graft copolymers with the identical chemical structure, that is, one mother PVA and one branch. However, according to the results given in Table 4-6, it is evident that the results of grafting are significantly different from one another. For instance the fraction of grafted PVA is increased as follows :

grafting by KPS > mutual irradiation >

pre-irradiation > without initiator.

The higher value of the fraction of grafted PVA in the chemical grafting than in the radiation-induced one may be explained from the above-mentioned fact. Namely, PVA has very reactive and hydrophilic groups similar to cellulose, and is able to form active redox system with various ions such as persulfate ions and metal ions (30). This redox system gives rise to production of polymer radicals, which initiate either graft or block copolymerization. On the other hand, it seems likely that for the less active polymers such as polyolefins the radiation methods are more advantageous than the chemical ones, since polymer radicals can be produced readily even from these polymers, if they are subjected to irradiation.

REFERENCES

1) For example, H. A. J. Battaerd and G. W. Tregear, Graft Copolymers, Interscience Publ., New York, 1967.
2) H. Yasuda, J. A. Wray, and V. Stannett, J. Polymer Sci. C, 2, 387 (1963).
3) V. Stannett, J. D. Wellons, and H. Yasuda, J. Polymer Sci. C, 4, 551 (1963).
4) J. D. Wellons, A. Schindler, and V. Stannett, Polymer [London], 5, 499 (1964).
5) R. Y.-M. Huang, J. Appl. Polymer Sci., 10, 325 (1966).
6) R. Y.-M. Huang and P. Chandramouli, J. Appl. Polymer Sci., 12, 2549 (1968).
7) R. Y.-M. Huang and P. Chandramouli, J. Polymer Sci., 7, 1393 (1969).
8) H. Sumitomo, S. Takakura, and Y. Hachihama, J. Chem. Soc. Japan, Ind. Chem. Sect. [Kōgyō Kagaku Zasshi] 66, 269 (1963).
9) H. Sumitomo and Y. Hachihama, J. Chem. Soc. Japan, Ind. Chem. Sect. [Kōgyō Kagaku Zasshi], 66, 1508 (1963).
10) J. Schurz, M. Rebek und H. Spörk, Angew. Makromolekulare Chem., 1, 42 (1967).
11) J. Tsurugi, T. Fukumoto, and K. Ogawa, Chem. High Polymers [Tokyo], 25, 116 (1968).
12) N. J. Morris, F. A. Blouin, and J. C. Arthur, J. Appl. Polymer Sci., 12, 373 (1968).
13) H. Langner, Makromolekulare Chem., 119, 37 (1968).
14) C. J. Hamburger, J. Polymer Sci., A-1, 7, 1023 (1969).
15) I. Sakurada, T. Okada, and E. Kugo, Isotopes and Radiation [Japan], 2, 296, 306, 316, 581 (1959) ; 3, 316, 329, 379, 406 (1960) ; 4, 240 (1961).
16) I. Sakurada, S. Matsuzawa and Y. Kubota, Makromolekulare Chem., 69, 115 (1963). See also the preceding papers.
17) I. Sakurada, Y. Ikada, and T. Yamaoka, Bull. Inst. Chem. Res., Kyoto Univ., 45, 1 (1967).
18) I. Sakurada, Y. Ikada, and Y. Uesaki, Bull. Inst. Chem. Res., Kyoto Univ., 47, 49 (1969).

19) Unpublished work.
20) M. Imoto, M. Kondo, and K. Takemoto, Makromolekulare Chem., 89, 165 (1965).
21) M. Imoto, K. Takemoto, and T. Otsuki, Makromolekulare Chem., 104, 244 (1967).
22) I. Sakurada, A. Nakajima, and H. Aoki, Memoirs Fac. Eng., Kyoto Univ., 21, 84 (1959).
23) Y. Sakaguchi and S. Funaya, Chem. High Polymers (Tokyo), 15, 677 (1958).
24) T. Naito and T. Kominami, Chem. High Polymers (Tokyo) , 11, 444 (1954).
25) D. Campbell, P. Ingram, J. L. Williams, and V. Stannett, J. Polymer Sci., B, 6, 409 (1968).
26) I. Sakurada, Y. Ikada, T. Yamaoka, and F. Horii, Bull. Inst. Chem. Res., Kyoto Univ., 46, 13 (1968).
27) I. Sakurada, Y. Ikada, and Y. Shima, presented at the 17th Annual Meeting of Soc. Polymer Sci. Japan, 1968.
28) I. Sakurada, Y. Ikada, and Y. Shima, presented at the 18th Annual Meeting of Soc. Polymer Sci. Japan, 1969.
29) I. Sakurada, Y. Ikada, and F. Horii, Bull. Inst. Chem. Res., Kyoto Univ., 47, 58 (1969).
30) W. A. Waters, Mechanisms of Oxidation of Organic Compounds, Methuen, London, 1964.

CHAPTER 5

COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS ON YIELD AND CHEMICAL STRUCTURE OF GRAFT COPOLYMERS

INTRODUCTION

In the previous chapters concerning the radiation grafting of vinyl monomers onto PVA, it was described that the number of grafted branches is about unity per one graft copolymer molecule, the fraction of grafted mother polymer being unexpectedly low. It seems of interest to discuss the experimental results from a theoretical view point. However, theoretical treatments on the grafting reaction have not yet been reported expect for quite simple cases (1,2). If some important quantities in the grafting, such as the fraction of the mother polymer participating in the grafting and the number of branches formed, can be predicted, studies on graft copolymerization will make great progress; for instance it may be easy to explore a method effective to increase the true grafting yield.

In this chapter fundamental quantities in graft copolymerization were calculated as a function of the probability of branch formation from the monomer residue of mother polymer and compared with the experimental results obtained in our laboratory. On the basis of the calculations, the structure of graft copolymer was also discussed and some efforts to increase the number of branches were attempted.

THEORETICAL

We deal with the graft copolymerization of a vinyl monomer initiated by radicals on a pre-existing mother polymer, leading to formation of a graft copolymer containing long sequences of two different monomer units. In the present treatment it is assumed that the grafted branches are formed randomly on the mother polymer and independently with each other. Production of active sites on mother substrate polymer via any secondary radicals is neglected. Furthermore the molecular weight of mother polymer is assumed not to change during graft copolymerization and to have a uniform or most probable distribution.

1. Probability of branch formation from a monomer residue (α)

α is generally given by the following equation ;

$$\alpha = \frac{f_b \int_0^t f_i \cdot R_d \cdot dt}{[M]_0} \qquad (5\text{-}1)$$

where $[M]_0$ is the concentration of monomer residue of mother polymer, f_b is the reacting efficiency of mother polymer radical with monomer, and t is the polymerization time (the pre-irradiation time in the case of pre-irradiation grafting). f_i and R_d are defined as follows according to the grafting method.

Case A : Chemical grafting

In a non-redox system, R_d is simply the rate of decomposition of catalyst and f_i is the reacting efficiency of catalyst radical with the mother polymer. In a redox initiation to which the mother polymer participates, R_d is similarly the rate of decomposition of catalyst, but represented as a function of the concentrations of catalyst and mother polymer. Here f_i is unity.

Case B : Radiation grafting

In both the mutual and pre-irradiation graftings, $f_i \cdot R_d / [M]_0$ is given by

$$\frac{f_i \cdot R_d}{[M]_0} = \frac{(G_a/100) \cdot I \cdot A}{N_A / M_{0,B}} \qquad (5\text{-}2)$$

where G_a is the G-value for the formation of active site, I is the dose rate(r/time), A is the energy conversion factor (= 5.8×10^{13} eV/g·r), N_A is Avogadro's number, and $M_{0,B}$ is the molecular weight of monomer residue of mother polymer. By substituting eq. (5-2) into eq. (5-1) and integrating it, we obtain

$$\alpha = \frac{f_b (G_a/100) R \cdot A}{N_A / M_{0,B}} = \frac{(1/100) \cdot A \cdot R (f_b \cdot G_a)}{N_A / M_{0,B}} \qquad (5\text{-}3)$$

where R(= I·t) is the radiation dose and $f_b \cdot G_a$ corresponds to the G-value for branch formation G_b. Hence we may write eq. (5-3) in the form

$$\alpha = 9.63 \times 10^{-13} R \cdot M_{0,B} \cdot G_b \qquad (5\text{-}4)$$

2. Number fraction of mother polymer with n branches (F_n)

2.1. Uniform distribution

Clearly F_n is given by

$$F_n = {}_P C_n \cdot \alpha^n (1 - \alpha)^{P-n} \qquad (5\text{-}5)$$

where P is the degree of polymerization of mother polymer.

2.2. Most probable distribution

By definition the number of mother molecules with P of the degree of polymerization, i(P), is

$$i(P) = (N/\bar{P}_{B,0}) \exp(-P/\bar{P}_{B,0}) \qquad (5\text{-}6)$$

where N is the total number of the monomer residues of mother polymer and $\bar{P}_{B,0}$ is the number average degree of polymerization of mother polymer. Then F_n is written in the form

$$F_n = \sum_{P=n}^{\infty} \frac{i(P) \cdot {}_P C_n \cdot \alpha^n (1 - \alpha)^{P-n}}{\sum_{P=1}^{\infty} i(P)}$$

$$= \frac{1}{\bar{P}_{B,0}} \sum_{P=n}^{\infty} \exp(-P/\bar{P}_{B,0}) \cdot {}_P C_n \cdot \alpha^n (1 - \alpha)^{P-n} \qquad (5\text{-}7)$$

If $n \ll P$ and $\alpha \ll 1$, F_n is given in a good approximation by

$$F_n = (\alpha \cdot \bar{P}_{B,0})^n / (1 + \alpha \cdot \bar{P}_{B,0})^{n+1} \qquad (5\text{-}7')$$

3. Weight fraction of mother polymer with n branches (W_n)

3.1. Uniform distribution

W_n is given by the same equation as eq. (5-5) ;

$$W_n = {}_P C_n \cdot \alpha^n (1 - \alpha)^{P-n} \qquad (5\text{-}8)$$

3.2. Most probable distribution

The general expression for W_n is

$$W_n = \sum_{P=n}^{\infty} \frac{P \cdot i(P)\,{}_PC_n \cdot \alpha^n (1-\alpha)^{P-n}}{\sum_{P=1}^{\infty} P \cdot i(P)}$$

$$= \frac{1}{(\bar{P}_{B,0})^2} \sum_{P=n}^{\infty} P \cdot \exp\,(P/\bar{P}_{B,0}) \cdot {}_PC_n \cdot \alpha^n (1-\alpha)^{P-n} \qquad (5\text{-}9)$$

If $n \ll P$ and $\alpha \ll 1$, it follows that

$$W_n = (n+1)(\alpha \cdot \bar{P}_{B,0})^n \,/\, (1 + \alpha \cdot \bar{P}_{B,0})^{n+2} \qquad (5\text{-}9')$$

4. Fraction of mother polymer grafted (f,w)

Number and weight fractions of mother polymer possessing, at least, one branch are given by the following equations, respectively :

$$f = \sum F_n = 1 - F_0 \qquad (5\text{-}10)$$

$$w = \sum W_n = 1 - W_0 \qquad (5\text{-}11)$$

where the summation should be taken from $n=1$ to P for the uniform distribution and from $n=1$ to ∞ for the most probable distribution. In the latter case, if $n \ll P$ and $\alpha \ll 1$, eqs. (5-10) and (5-11) reduce to

$$f = \alpha \cdot \bar{P}_{B,0} \,/\, (1 + \alpha \cdot \bar{P}_{B,0}) \qquad (5\text{-}10')$$

$$w = \alpha \cdot \bar{P}_{B,0}(2 + \alpha \cdot \bar{P}_{B,0}) \,/\, (1 + \alpha \cdot \bar{P}_{B,0})^2 \qquad (5\text{-}11')$$

5. Average number of branches grafted per one mother polymer molecule (N_t)

In general N_t is given by

$$N_t = \sum n \cdot F_n \qquad (5\text{-}12)$$

where the summation is taken over in the same way as in eqs.(5-10) and (5-11). By substituting eq. (5-5) or (5-7') into eq. (5-12),

we obtain the following equation regardless of the type of molecular weight distribution;

$$N_t = \alpha \cdot \bar{P}_{B,0} \qquad (5\text{-}12')$$

6. Average number of branches grafted per one mother polymer molecule (N_g)

N_g is given by the following equation for the most probable molecular weight distribution;

$$N_g = \sum_{n=1}^{\infty} n \cdot F_n \Big/ \sum_{n=1}^{\infty} F_n = 1 + N_t \qquad (5\text{-}13)$$

However if the molecular weight distribution is uniform, the summation should be carried out from n=1 to P.

It can be shown that N_g is related to w as follows:

$$N_g = -\ln (1 - w) / w \quad \text{(uniform distribution)} \qquad (5\text{-}14)$$

$$N_g = (1 - w)^{-1/2} \quad \text{(most probable distribution)} \qquad (5\text{-}15)$$

7. Average degree of polymerization of the backbone with n branches

If the mother polymer has a most probable molecular weight distribution, the number average degree of polymerization $\bar{P}_{B,n}$ of the backbone with n branches is given by

$$\bar{P}_{B,n} = \frac{\sum_{P=n}^{\infty} P \cdot i(P) \cdot {}_PC_n \cdot \alpha^n (1 - \alpha)^{P-n}}{\sum_{P=n}^{\infty} i(P) \cdot {}_PC_n \cdot \alpha^n (1 - \alpha)^{P-n}} \qquad (5\text{-}16)$$

The weight average degree of polymerization $\bar{P}^{W}_{B,n}$ of the backbone with n branches is

$$\bar{P}^{W}_{B,n} = \frac{\sum_{P=n}^{\infty} P^2 \cdot i(P) \cdot {}_PC_n \cdot \alpha^n (1 - \alpha)^{P-n}}{\sum_{P=n}^{\infty} P \cdot i(P) \cdot {}_PC_n \cdot \alpha^n (1 - \alpha)^{P-n}} \qquad (5\text{-}17)$$

When $n \ll P$ and $\alpha \ll 1$, eqs.(5-16) and (5-17) reduce to eqs.(5-16') and (5-17') in a good approximation;

$$\bar{P}_{B,n} = \left[(n + 1)/(1 + \alpha \cdot \bar{P}_{B,0})\right] \cdot \bar{P}_{B,0} \qquad (5\text{-}16')$$

$$\bar{P}^{W}_{B,n} = \left[(n + 2)/(1 + \alpha \cdot \bar{P}_{B,0})\right] \cdot \bar{P}_{B,0} \qquad (5\text{-}17')$$

8. Average degree of polymerization of the backbone of graft copolymer

For the graft copolymer whose mother polymer has a most probable molecular weight distribution, the number and weight average degrees of polymerization of the whole backbone having branches, $\bar{P}_{B,g}$ and $\bar{P}^{W}_{B,g}$, are given by the following equations;

$$\bar{P}_{B,g} = \frac{\sum_{n=1}^{\infty} \sum_{P=n}^{\infty} P \cdot i(P) \cdot {}_{P}C_{n} \cdot \alpha^{n} (1 - \alpha)^{P-n}}{\sum_{n=1}^{\infty} \sum_{P=n}^{\infty} i(P) \cdot {}_{P}C_{n} \cdot \alpha^{n} (1 - \alpha)^{P-n}} \qquad (5\text{-}18)$$

$$\bar{P}^{W}_{B,g} = \frac{\sum_{n=1}^{\infty} \sum_{P=n}^{\infty} P^{2} \cdot i(P) \cdot {}_{P}C_{n} \cdot \alpha^{n} (1 - \alpha)^{P-n}}{\sum_{n=1}^{\infty} \sum_{P=n}^{\infty} P \cdot i(P) \cdot {}_{P}C_{n} \cdot \alpha^{n} (1 - \alpha)^{P-n}} \qquad (5\text{-}19)$$

If $n \ll P$ and $\alpha \ll 1$, we obtain the following equations as very close approximations,

$$\bar{P}_{B,g} = \left[(2 + \alpha \cdot \bar{P}_{B,0})/(1 + \alpha \cdot \bar{P}_{B,0})\right] \cdot \bar{P}_{B,0} \qquad (5\text{-}18')$$

$$\bar{P}^{W}_{B,g} = \frac{(6 + 6\alpha \cdot \bar{P}_{B,0} + 2(\alpha \cdot \bar{P}_{B,0})^{2}}{(1 + \alpha \cdot \bar{P}_{B,0})(2 + \alpha \cdot \bar{P}_{B,0})} \cdot \bar{P}_{B,0} \qquad (5\text{-}19')$$

The ratio $\bar{M}_{w}/\bar{M}_{n}$ is often used as a measure of the polydispersity of a polymer sample. By using eqs.(5-18') and (5-19'), the ratio of the backbone polymer of graft copolymer is given by

$$\frac{\overline{P}^{W}_{B,g}}{\overline{P}_{B,g}} = \frac{(6 + 6\alpha\cdot\overline{P}_{B,0} + 2(\alpha\cdot P_{B,0})^2)}{(2 + \alpha\cdot\overline{P}_{B,0})^2} \qquad (5\text{-}20)$$

9. Number fraction of graft copolymer with n branches ($F_{g,n}$)

$$F_{g,n} = \frac{\sum_{P=n}^{\infty} i(P)\cdot {}_PC_n\cdot\alpha^n(1-\alpha)^{P-n}}{\sum_{n=1}^{\infty}\sum_{P=n}^{\infty} i(P)\cdot {}_PC_n\cdot\alpha^n(1-\alpha)^{P-n}} \quad \text{(most probable distribution)} \qquad (5\text{-}21)$$

10. Weight fraction of graft copolymer with n branches ($W_{g,n}$)

As mentioned above, it is assumed that the growth of each branch is not affected by the position on the backbone polymer and the existence of other branches. Then $W_{g,n}$ is given by

$$W_{g,n} = \frac{\sum_{P=n}^{\infty}(M_{OB}P + nM_{Ob}\overline{P}_b)\cdot i(P)\cdot {}_PC_n\cdot\alpha^n(1-\alpha)^{P-n}}{\sum_{n=1}^{\infty}\sum_{P=n}^{\infty}(M_{OB}P + nM_{Ob}\overline{P}_b)\cdot i(P)\cdot {}_PC_n\cdot\alpha^n(1-\alpha)^{P-n}}$$

(most probable distribution) (5-22)

where $\overline{P}_b$ and M_{Ob} are the number average degree of polymerization and the molecular weight of monomer residue of branch polymer, respectively. When $n \ll P$, $\alpha \ll 1$ and $M_{OB}=M_{Ob}$, we obtain

$$W_{g,n} = \frac{\left[n\cdot\overline{P}_b + (n+1)L\right](L\alpha)^{n-1}(1-L\alpha)^2}{\overline{P}_b + L(2-L\alpha)} \qquad (5\text{-}22')$$

where $L = \overline{P}_{B,0}/(1 + \alpha\cdot\overline{P}_{B,0})$.

RESULTS

The above equations are mainly expressed in terms of α and $\bar{P}_{B,0}$ or N_t and N_g which are a function of α and $\bar{P}_{B,0}$, as is seen from eq. (5-12') or (5-13). Therefore the knowledge on the magnitude of α or N_t is necessary to evaluate the grafting yield or the number of branches with the employment of the above equations.

In the radiation grafting N_t is given from eqs. (5-12') and (5-4) by

$$N_t = \alpha \cdot \bar{P}_{B,0} = 9.63 \times 10^{-13} R \cdot M_{OB} \cdot G_b \cdot \bar{P}_{B,0}$$

$$= 9.63 \times 10^{-13} R \cdot \bar{M}_{B,0} \cdot G_b \qquad (5\text{-}23)$$

where $\bar{M}_{B,0}$ is the number average molecular weight of mother polymer. Relationships between N_t and R are shown in Fig. 5-1 for various G_b-values at $\bar{M}_{B,0} = 10^5$. Since the G-value for radical formation on mother polymer, which is considered to be comparable to the G_b-value, is about 0.1 to 10 for most of polymers and the dose employed in usual radiation graftings is 10^5 to 10^6 r, N_t may be lower than 1.0. On the other hand the prediction of N_t in chemical graftings is much difficult, but it seems possible to raise N_t to much higher than unity.

Taking into account this evaluation, the weight fraction of backbone polymer with n branches W_n was calculated as a function of N_t. In Figs. 5-2 and 5-3 are shown the results for the mother polymers possessing uniform and most probable molecular weight distribution, respectively. As clearly seen, the distributions of W_n become broader with increasing N_t. The influence of molecular weight distribution is negligible at low N_t, but becomes prominent at high N_t. It is noteworthy that the weight fraction of mother polymer with one branch does not exceed 0.2 and that of two branches is very low, as far as N_t remains 0.01 to 0.1 as in the usual radiation grafting.

Fig. 5-4 shows a relationship between the weight fraction of

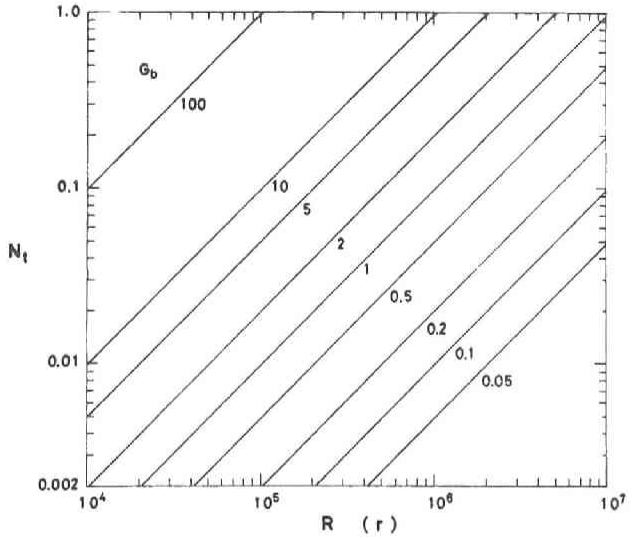


Fig. 5-1. Relationship between radiation dose(R) and average number of branch formed per one mother polymer molecule (N_t) ($M_{B,0} = 10^5$)

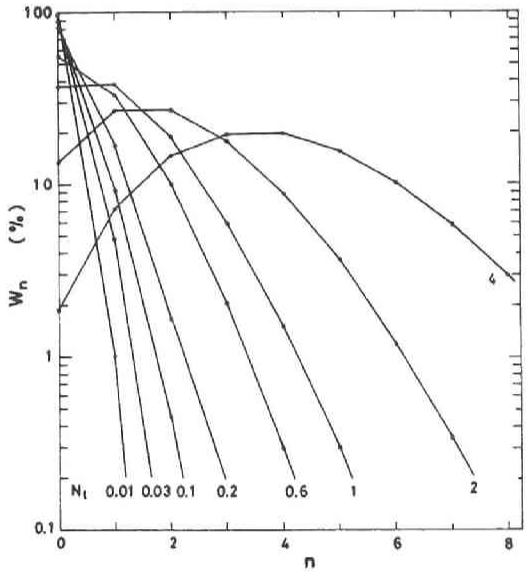


Fig. 5-2. Weight fraction of mother polymer with n branches (W_n) : uniform distribution.

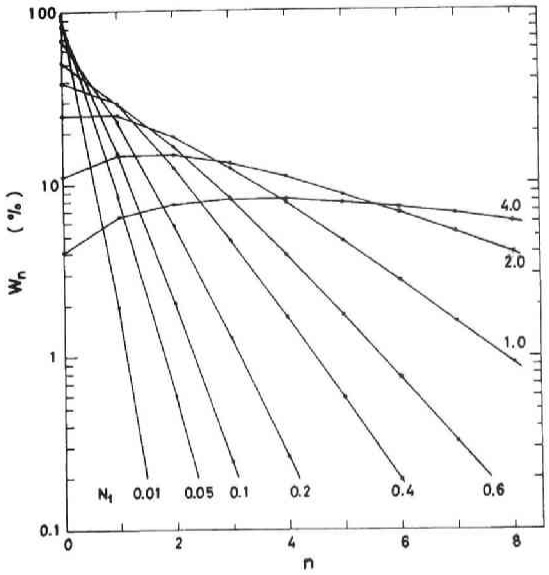


Fig. 5-3. Weight fraction of mother polymer with n branches (W_n) : most probable distribution.

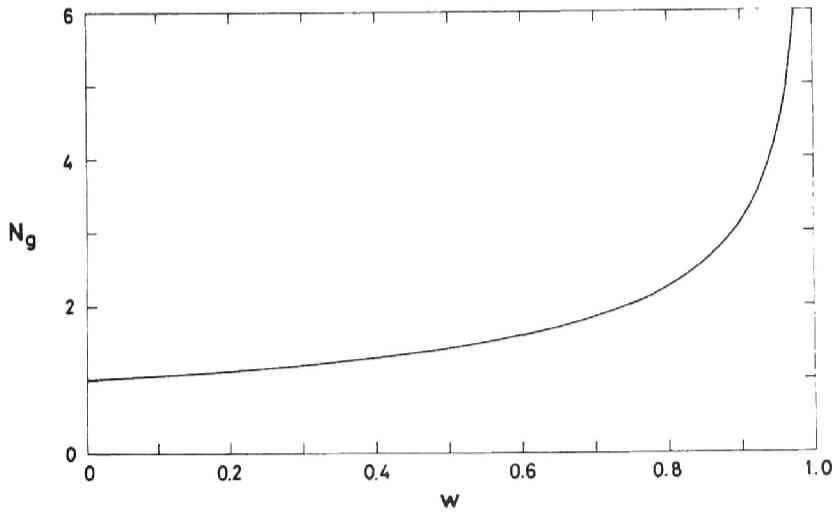


Fig. 5-4. Relationship between weight fraction of grafted mother polymer (w) and average number of branch per one graft copolymer molecule (N_g).

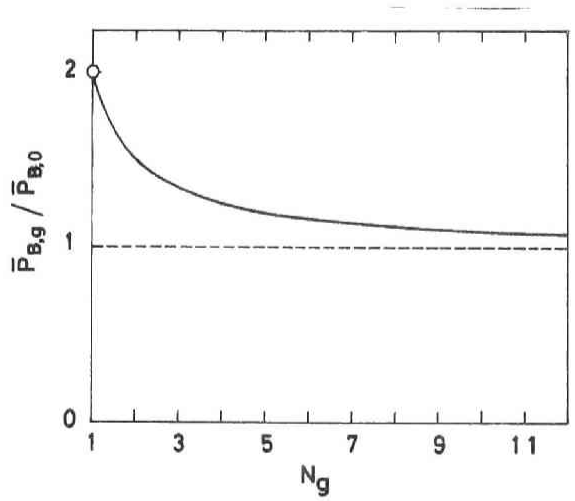


Fig. 5-5. Relationship between $\bar{P}_{B,g}/\bar{P}_{B,0}$ and average number of branches grafted per one graft copolymer(N_g).

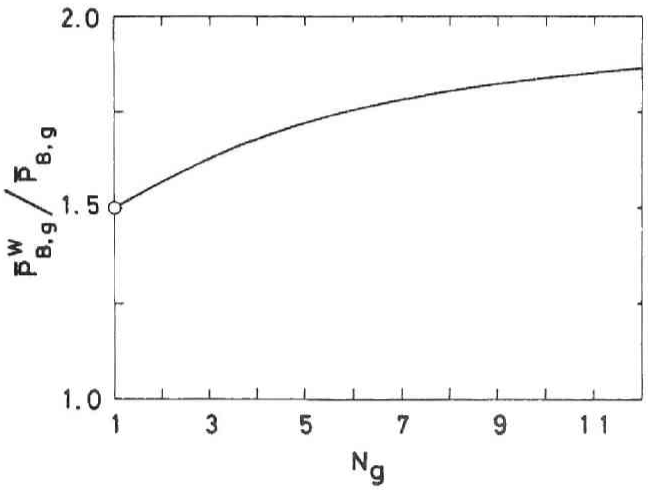


Fig. 5-6. Polydispersity of the backbone of graft copolymers with various branches.

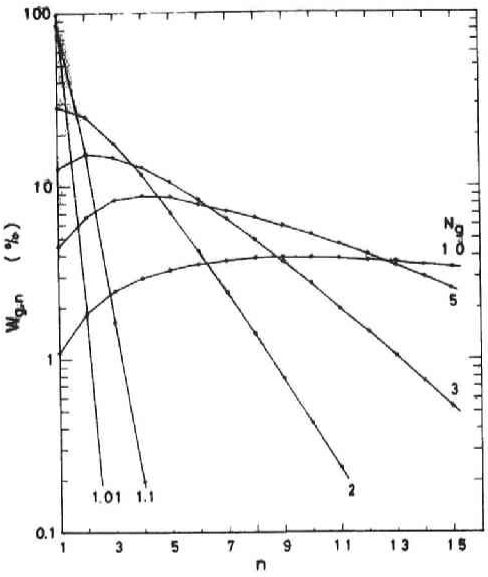


Fig. 5-7. Weight fraction of graft copolymer with n branches.

grafted mother polymer w and the average number of branches N_g per one graft copolymer molecule according to eqs.(5-14) and (5-15). The difference of N_g-w relationship between the uniform and most probable distribution is negligible. It is obvious that the graft copolymer with more than 2 branches on the average cannot be produced unless w becomes higher than 0.75, which is, however, hardly attainable at the usual radiation grafting.

A relationship between $\overline{P}_{B,g}/\overline{P}_{B,0}$ and N_g was shown in Fig.5-5 according to eq.(5-18'). It can be seen that $\overline{P}_{B,g}/\overline{P}_{B,0}$ has a value of about 2, if N_g is close to unity.

The polydispersity of the backbone of graft copolymers was given in Fig. 5-6, where the ratio $\overline{P}^{W}_{B,g}/\overline{P}_{B,g}$ was plotted against N_g according to eq.(5-20). The ratio is seen to increase from 1.5 to 2 with the increase of N_g.

In Fig. 5-7 the weight fraction of graft copolymer was plotted against the number of branches according to eq. (5-22') for various N_g values. Here $\overline{P}_B$ and $\overline{P}_b$ were assumed to be 1000. It is clear that most of graft copolymer have only one branch, if N_g is close to unity.

DISCUSSION

1. Grafting yield

In Tables 5-1 and 5-2 are summarized the conditions and the results of the radiation graftings shown in the previous chapters together with those reported elsewhere (3-5). The grafting condition was in every case selected so that side reactions can be suppressed to a negligible extent whereas the weight increase becomes as high as possiole. The mother polymers were used without fractionation except for sample M1M.

As clearly seen from Table 5-2, the yield in the grafting without irradiation is by far lower than that in the corresponding radiation graftings. This suggests that graft copolymer is formed predominantly as a result of gamma-ray irradiation. In each radiation grafting the fraction of mother polymer grafted is lower than 0.1. This agrees fairly well with the theoretical expectation. The difference between mutual and pre-irradiation graftings is evidently characterized by the fact that the grafting efficiency of the latter is always higher than that of the former.

In order to express the grafting yield, several experimental values can be utilized : the percent graft, the fraction of grafted mother polymer and the G_b-value of graft branch formation. The two formers depend not only on the radiation dose, but also on the molecular weights of branch and mother polymer. Therefore it seems more appropriate to use the G_b-value, since it is theoretically independent of the radiation dose and any molecular weights.

The G_b-value of branch formation, defined as the total number of graft branches produced by irradiation of 100 eV, is given by the following equation, if grafting takes place uniformly throughout the cross section of films or fibers.

$$G_b = Y \cdot N_A \; / \; R \cdot A \cdot \bar{M}_{n,b} \qquad (5\text{-}24)$$

Here Y is the percent graft and $\bar{M}_{n,b}$ is the number average molecular weight of grafted branch. G_b-values calculated by using eq. (5-24) are summarized in Table 5-3 with the G_R-values of radical formation on PVA(6,7), cellulose(8,9) PET(10) and nylon(11) re-

Table 5-1. Conditions of graft copolymerization

Backbone polymer	PVA				Cellulose	PET[a]		Nylon	
Monomer	MMA			St	St	St		St	
Grafting method	M[b),d)] (M1M)	P[c)]	Without[e)] irrad.	M[b),d)] (M4S)	M[b)]	M[b)]	P[c)]	M[b)]	P[c)]
Monomer / MeOH (vol.)	20/80	40/60	40/60	20/80	20/72[f)]	50/50	50/50	50/50	50/50
[Chain transfer agent] / [Monomer] (mol.)	0.5	0.5	0.5	0.05	0.05	0.05	0.05	0.05	0.05
Dose rate (10^4) (rad/hr)	0.61	6.6	—	1.0	1.0	1.0	17	0.83	17
Dose (Mrad)	0.30	1.0	—	0.46	0.20	0.50	14	0.39	2.4
Polym. temp. (^{o}C)	50	50	60	50	50	50	50	50	20

a) Poly(ethylene terephthalate), b) Mutual irradiation, c) Pre-irradiation,

d) Pre-swollen with H_2O-MeOH(40 : 60) to a degree of swelling of 1.64.

e) " H_2O " 2.64.

f) H_2O was added. Monomer / MeOH / H_2O = 20/72/8.

Table 5-2. Results of graft copolymerizations

Backbone polymer	PVA				Cellulose	PET		Nylon	
Monomer	MMA			St	St	St		St	
Grafting method	M (M1M)	P	Without irrad.	M (M4S)	M	M	P	M	P
Total conversion of monomer (%)	100	18.4	14.8	100	34.3	100	15.4	100	27.1
Percent graft (%)	18.9	18.1	1.9	11.1	11.0	0.47	3.43	6.2	14.6
Graft efficiency (%)	2.3	10.2	1.8	2.0	6.36	0.14	10.3	1.7	27.3
Frac. of grafted mother polymer(%)	10.9	4.25	0.46	6.4	4.95	0.043	0.56	0.54	1.38

Table 5-3. G-values of branch formation and numbers of branches in one graft copolymer molecule

Backbone polymer	PVA				Cellulose	PET		Nylon	
Monomer	MMA			St	St	St		St	
Grafting method	M (M1M)	P	Without irrad.	M (M4S)	M	M	P	M	P
G-value									
branch formation	3.6	0.3	——	1.3	3.1	0.05	0.01	0.70	0.17
radical "		1-6 ,	8.0		2.9	0.025		0.7	
Ref.		(6)	(7)		(8,9)	(10)		(11)	

ported by other investigators. As is clearly seen, the G_b-value at the pre-irradiation grafting is lower than that at the mutual grafting. This result may be ascribed to partial disappearance of radicals before they initiate the polymerization of monomer, and furthermore, especially in the pre-irradiation grafting onto PVA films, to the fact that the grafting is restricted near the film surface.

It is interesting to point out that the G_b-value is almost equivalent to G_R, at least in the order of magnitude, though one should not place too much emphasis on the absolute values of G_R as well as G_b owing to the dependence of G_R-value on the hysteresis of polymer sample and the method of measurement. It is sure that this equivalency is not a result of the existence of a chain transfer agent used as a modifier of the length of grafted branch, because the G_b-value is not affected by the chain transfer agent as made clear in Chapter 3. Thus the number of branches formed by the radiation grafting can be regarded to closely relate to the number of active sites formed by irradiation. In other words, the maximum grafting yield can be roughly predicted from the G_R-value of radical formation on the mother polymer.

2. Chemical structure of graft copolymers

The chemical structure of graft copolymers produced by the radiation grafting is summarized in Table 5-4. The number of branches was calculated by

$$\text{average number of branches} = \frac{\bar{M}_n \text{ of branch part in graft copolymer}}{\bar{M}_n \text{ of isolated branch}}$$

$$= \frac{\left(\bar{M}_n \text{ of graft copolymer}\right) \times \left(\text{wt. fraction of branch part of graft copolymer}\right)}{\bar{M}_n \text{ of isolated branch}} \qquad (5\text{-}25)$$

Table 5-4. Molecular weights and chemical structures of graft copolymers

Backbone polymer	PVA[a)]				Cellulose[a)]	PET		Nylon	
Monomer	MMA			St	St	St		St	
Grafting method	M (M1M)	P	Without irrad.	M (M4S)	M	M	P	M	P
MMA or St cont. of graft copolymer (wt%)	47.2	61.4	68.8	63.5	55.8	91.5	85.9	91.9	91.4
$\bar{M}_n \times 10^{-5}$ graft copolymer	4.17	6.65	6.88	3.90	3.06	2.20	1.90	2.89	3.87
$\bar{M}_n \times 10^{-5}$ mother backbone	1.84	1.15	1.15	1.15	0.724	0.197	0.197	0.153	0.153
$\bar{M}_n \times 10^{-5}$ separated branch	1.81	4.42	5.32	1.88	1.87	2.03	2.00	2.37	3.71
Number of branches	1.09	0.93	0.89	0.97	0.92	0.99	0.82	1.12	0.95
$\bar{M}_B/\bar{M}_{B,0}$	1.20	2.23	1.87	1.80	1.87	0.95	1.36	1.56	2.22

a) Hydroxyl groups in the polymers were completely acetylated.

It is evident that the average number of branches is about unity in every case. This result accords with the theoretical evaluation shown in Fig. 5-4. Since the G_R-value of most of polymers is smaller than 10, it cannot be expected that a graft copolymer prepared by the radiation grafting has more than 2 branches on the average.

The ratios of the number average molecular weight of the backbone part($\bar{M}_B$) to that of the mother polymer($\bar{M}_{B,0}$) which were calculated by the following equation are also given in Table 5-3.

$$\bar{M}_B / \bar{M}_{B,0} = \frac{\bar{M}_n \text{ of backbone part in graft copolymer}}{\bar{M}_n \text{ of mother polymer}}$$

$$= \frac{\left(\bar{M}_n \text{ of graft copolymer}\right) \times \left(\text{wt. fraction of backbone part of graft copolymer}\right)}{\bar{M}_n \text{ of mother polymer}} \qquad (5\text{-}26)$$

It is seen that the ratio is close to two in the case of graft copolymers prepared from the unfractionated mother polymers(PVA, cellulose and nylon), whereas about unity for the PVA-MMA graft copolymer(M1M) prepared from the fractionated mother PVA. Besides, the ratios were found to be 1.69 and 2.08 for samples M3M and M7M prepared under the same conditions as sample M1M except for the use of the unfractionated PVA's with $\bar{M}_{B,0}=3.40 \times 10^4$ and 5.89×10^4, respectively. When the mother polymer has a most probable molecular weight distribution and the number of branches is around unity, the ratio $\bar{M}_B/\bar{M}_{B,0}$ should be close to 2 as shown in Fig. 5-5. Therefore the observed ratios coincide fairly well with the theoretical. It appears that the low ratios observed for the PET-styrene graft copolymers may be due mainly to the molecular weight distribution of mother PET which is different from the most probable one.

The good agreement between the experimental and theoretical results indicates that the products are not block type but graft one. If the end of mother polymer is preferentially activated and a block copolymer is formed, $\bar{M}_B / \bar{M}_{B,0}$ should not be equal to 2 but unity regardless of N_g value.

3. Preparation of graft copolymer possessing numerous branches

To increase the number of branches, the weight fraction of grafted mother polymer must be enhanced as is clear from Fig. 5-4. In radiation grafting, R, f_b and G_a must be increased for this purpose, as eqs. (5-11') and (5-3) suggest. From an experimental view point one can easily increase R. However side reactions such as degradation or closslinking of mother polymer may occur on irradiation at a high dose. In the mutual grafting the supply of monomer may become insufficient at a high dose owing to the consumption for the homopolymerization. The second possibility is to enhance the reaction efficiency, that is, f_b. However it is evident from the work in Chapter 3 that such solvents as swelling agents and chain transfer agents are not so much effective to increase f_b. Another method to increase the branch number is to raise G_b by chemical modification of the mother polymer, for instance, by introduction of groups which are apt to form radical. This may cause also the enhancement of the chain transfer to mother polymer, giving rise to the increase of branch number. Any effort has not been paid toward this problem.

Since the catalyst concentration can be easily increased, the number of branch is expected to increase at the chemical grafting, though side reactions may also occur. Thus the grafting of MMA onto PVA films using potassium persulfate(KPS) as an initiator was investigated. However, as shown in Chapter 4, good results were not obtained, because KPS was insufficiently penetrated into PVA films. Therefore we carried out a homogeneous grafting by using dimethyl sulfoxide(DMSO) as a common solvent for PVA and PMMA. A certain amount of KPS and 18 ml of MMA were added to PVA-DMSO solution(2 g/60 ml) in a test tube. After degassing the solution, the test tube was sealed. The reaction was allowed to

Table 5-5. Graft copolymerization of MMA onto PVA in DMSO solution by patassium persulfate (PVA = 2.5 wt%, MMA = 22.5 wt%, wt.of starting PVA = 2 g and $\bar{M}_n$ of starting PVA = 5.9×10^4).

Exp. no.	DG-1	DG-2	DG-3	DG-4	DG-5	DG-6
Polym. temp. (^oC)	60	40	60	60	30	80
KPS (wt%)	0.31	0.06	0.81	0.06	0.31	0.31
Reac. time (hr)	2	41	2	2	15.5	2
Graft copolymer	soluble	soluble	colored, insoluble	soluble	soluble	insoluble
MMA content of acetylated GP (wt%)	58.6	71.7		65.4	71.8	
$\bar{M}_n \times 10^{-4}$ Acetylated GP	36.5	109		61.2	85.1	
$\bar{M}_n \times 10^{-4}$ Branch	5.37	19.9	polymer permeated membrane	15.2	19.5	not recovered
Number of branches	3.6	3.9		2.6	3.1	
$\bar{M}_B/\bar{M}_{B,0}$	1.32	2.75		1.84	2.09	

proceed for a certain time interval at a given temperature from 30 to 80°C. The methods of isolation and characterization of the graft copolymer were the same as described in Chapter 4. The results are given in Table 5-5. It is seen that the graft copolymers having about 2 to 4 branches are obtained. The weight fraction of PVA grafted was higher than 0.8 in every case except for DG-3 and DG-6, though the value could not be distinctly determined because of the loss of the graft copolymer into the extracting solvents. On the other hand, side reactions became predominant, when the reaction condition was severe as in the cases of DG-3 and DG-6.

Table 5-6. Repeated radiation graft copolymerization of MMA onto PVA [swelling : in water-MeOH(40-60), monomer solution : MMA-MeOH(20-80), [trichloroethylene]/[MMA] = 0.5(by mole), irradiation : 50°C, dose = 2.63 x 10^5r].

Grafting		1st (M2M)	2nd	3rd
Final solvent for extraction prior to the next grafting		——	water	benzene
Weight of polymer to be irradiated	(g)	20.46	2.00	2.148
PVA content in the polymer	(g)	20.46	0.778	0.778
Apparent weight increase	(g)	42.74	0.219	0.339
"	(%)	309	10.9	15.8
Weight of branch PMMA formed	(g)	2.93	0.148	- 0.003
Instantaneous percent graft	(%)	14.3	7.4	0
Cumulative "	(%)	14.3	16.1	16.1
Total conversion of monomer	(%)	94	88	82

Terefore this method may be also restricted to the preparation of graft copolymer with only several branches.

Another possibility to increase the number of branches is to repeat grafting reaction with the same sample. The results of the repeated mutual grafting of MMA onto PVA are summarized in Table 5-6. The graftings at the second and the third step were carried out under the same condition as the first (M2M) for the graft copolymer freed from the homopolymers. It is evident from the table that the further grafting hardly took place at the third step, though the first and the second graftings occurred to a significant extent. This result may chiefly be due to the difficulty of the MMA monomer to diffuse into the crystalline part of PVA.

REFERENCES

1) T. Alfrey, Jr. and C. Lewis, J. Polymer Sci., 4, 767 (1949).
2) F. Merrett, Trans. Faraday Soc., 50, 759
3) I. Sakurada, Y. Ikada, and Y. Nishizaki, J. Polymer Sci., C, 37, 265 (1972).
4) Y. Ikada, T. Kawahara, and I. Sakurada, presented at the 18th Polymer Symposia of Polymer Soc., Japan, 1969, Preprint, p.243. (J. Polym. Sci., Polym. Chem. Ed., 11, 2329 (1973))
5) Y. Ikada, T. Kawahara, F. Horii, and I. Sakurada, presented at 19th Polymer Symposia of Polymer Soc., Japan, 1970, Preprint, p.519.(J. Polym. Sci., Polym Chem. Ed., 11,2329(1973))
6) F. Kimura-Yeh, private communication.
7) S. Ohnishi, Bull. Chem. Soc. Japan, 35, 254 (1962).
8) R. E. Florin and L. A. Wall, J. Polymer Sci., A, 1, 1163 (1963).
9) J. T. Guthrie, M. B. Huglin, and G. O. Phillips, J. Polymer Sci., C, 37, 205 (1972).
10) D. Campbell and D. T. Turner, J. Polymer Sci., A-1, 5, 2199 (1967).
11) C. T. Graves and M. G. Ormerod, Polymer, 4, 81 (1963).

CHAPTER 6

ISOLATION OF GRAFT COPOLYMER FROM THE REACTION PRODUCT

INTRODUCTION

In general, grafting products contain more or less the corresponding homopolymers. Therefore, in order to obtain the pure graft copolymer it is essential to remove the homopolymers from the crude product. Nevertheless, only a few papers(1-8) have been published which include the careful isolation. The most probable reason is that the isolation is not simple. For instance, the isolation procedure is awfully cumbersome for the products of radiation-induced graftings, where the fraction of the mother polymer participating in the grafting is rather low and also the homopolymer corresponding to the branch is formed by a large amount as shown in the previous chapters. In addition, we are apt to suppose that the isolation has been effected sufficiently enough before the true isolation is completed, as mechanical mixtures of two homopolymers can be easily separated in most cases. It should be also mentioned that there has been no good means to estimate the purity of the graft copolymer except for the density gradient centrifugation(9) which requires, however, a complicated technique and a device.

In this chapter we will discuss several problems relating to the isolation process based on our experimental results and present effective isolation methods, especially noting the emulsifying effect of graft copolymers on the isolation. Finally we will estimate the purity of isolated graft copolymers by means of thin-layer chromatography. For an illustrative purpose attention will be confined to the graft copolymers with one branch, but the similar consideration may apply to those with many branches and block copolymers.

ISOLATION METHODS

The methods generally utilized to isolate the graft copolymer from the reaction product can be, in principle, divided into three

groups. They are selective precipitation, extraction, and adsorption chromatography methods.

1) Selective precipitation

The selective precipitation is usually carried out with the intention to precipitate only one homopolymer, say poly-A, from the solution of a crude reaction product by adding a precipitant for poly-A. The separation by this method seems to give a successful result, since the poly-A-B graft copolymer can be held in the solution as dispersed micelle(10). However, it is usually observed(1,11) that on addition of the precipitant a stable dispersion is formed which can not be coagulated to a complete extent even by long centrifugation at relatively high gravities.

This phenomenon may be interpreted as follows: with addition of the precipitant, not only the poly-A homopolymer but also the poly-A sequence in the graft copolymer molecule collapse and form the core of the micelle. The other, soluble sequences may form a peripheral outer shell of the micelle. In other words, the graft copolymer is considered to act as an emulsifier of poly-A homopolymer. This emulsification is schematically represented in Fig. 7-10. As shown in Chapter 7, the homopolymer to be precipitated was completely emulsified, for example, by a graft copolymer of 15 wt.% based on the homopolymer. Accordingly it is concluded that such a method as intended to precipitate selectively only one homopolymer does not give the true value owing to the emulsifying behavior of the coexisting graft copolymer.

However, if it is possible to coprecipitate the graft copolymer with poly-A, keeping poly-B alone in the solution, we may be able to remove poly-B from the reaction product. For this purpose the solubility of poly-A-B graft copolymer should sufficiently differs from that of poly-B. As an example, turbidimetric titration curves of polystyrene (PS), poly(vinyl acetate) (PVAC), and PVAC-styrene graft copolymer (M4S) isolated from a radiation-grafting product are shown in Fig. 6-1. The turbidity was measured by adding water, a common non-solvent, to each dioxane solution of about 5 mg/dl at room temperature. The result indicates clearly that the graft copolymer is completely coagulated

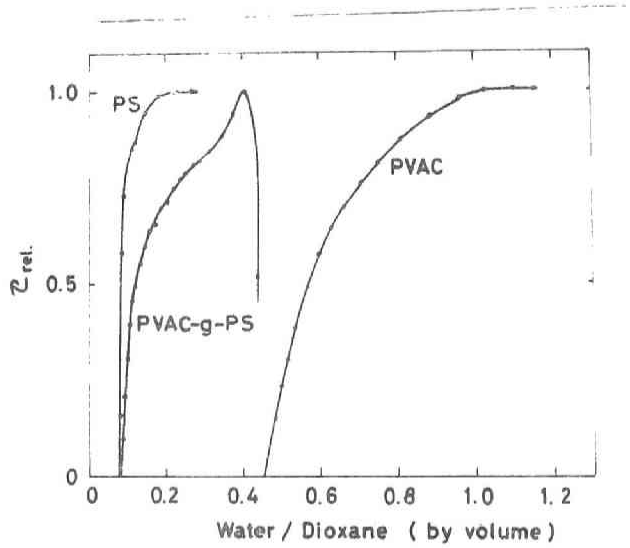


Fig. 6-1. Turbidimetric titration curves of PS, PVAC, and PVAC-styrene graft copolymer.

before the PVAC homopolymer begins to be precipitated, suggesting our proposed method to be promising. The detailed study on the micelle coagulation will be given in Chapter 9.

Table 6-1 gives a typical result of this modified precipitation performed for a physical mixture of PVAC, PS, and PVAC-styrene graft copolymer (M4S) (1 : 1 : 0.5). The mixture was dissolved in dioxane and precipitated selectively by adding water by such an amount as PS was completely precipitated but PVAC was still in a dissolved state. After the solution containing the precipitate was subjected to centrifugation at a high speed, the PVAC homopolymer was recovered by evaporation of the solvent from the supernatant solution. As seen in Table 6-1, only about half of the added PVAC homopolymer was separated by the first precipitation procedure. However, the coprecipitated PVAC homopolymer could be removed by repetition of the re-solution and re-precipitation procedure for the precipitate. In this experiment the separation was accomplished after 6 repetition. The number of repetition required for the complete separation would decrease if the precipitant is added by the amount as small as just to coagulate the graft copolymer and as slowly as possible. When the amount of the precipitant was too insufficient to coagulate

Table 6-1. Removal of PVAC from a PVAC - PS - PVAC-styrene graft copolymer mixture by the modified precipitation (initial polymer conc. ≒ 2 g/dl)

Precipitation	Water / Dioxane (by vol.)	Recovered PVAC	
		Weight (mg)	Cumulative wt. fraction
1	0.35	51.4[a)]	0.514
2	0.35	25.3[a)]	0.767
3	0.365	3.9	0.806
4	0.35	18.5[a)]	0.991
5	0.36	0.5	0.996
6	0.36	0.6	1.002

a) Styrene unit was not detected in the IR spectra.

completely the graft copolymer, the supernatant appeared more or less turbid even after the centrifugation. The removal of PS homopolymer from the PVAC - PS - PVAC-g-PS mixture was also successful when dioxane - n-hexane was used as a solvent - precipitant system.

The modified precipitation was further attempted for the product obtained by radiation grafting of styrene onto cellulose(12). After the cellulose part was completely acetylated to triacetate, the product was dissolved in a mixture of methylene chloride - methanol (80 : 20) and then methanol was added to precipitate selectively the PS homopolymer and the graft copolymer. The result of the precipitation is given in Table 6-2. It can be seen from the table that the removal of the unreacted cellulose triacetate (CTA) came virtually to completion after the precipitation procedure was repeated four times. The recovered precipitate could be easily separated into the PS homopolymer and the graft copolymer by extraction of the former with benzene. As will be described later, it was confirmed by thin-layer chromatography

Table 6-2. Removal of unreacted CTA from the graft product by modified precipitation ; methylene chloride - methanol (acetylated grafting product = 5.00 g[b]).

Precipitation	Initial polymer conc. (wt%)	CH_3OH cont. of final solution (vol%)	Recovered CTA	
			Weight (g)	Cumulative wt. fraction
1	2.0	45.0	2.287[a]	0.572
2	2.7	45.0	1.139[a]	0.856
3	3.9	46.3	0.084[a]	0.877
4	4.3	46.3	0.014	0.881

a) Styrene unit was not detected in the IR spectra.
b) The weight of total CTA in cluding the backbone of graft copolymer and the homopolymer is 3.99 g.

that the separation of the three component polymers was satisfactorily carried out.

Form the above results it may be concluded that the separation by the precipitation technique is effective if carried out in such a way poly-A and poly-A-B graft copolymer are coprecipitated and only poly-B is left in solution. The clear phase separation observed by Merrett(1) and Magat et al.(3) in the isolation of graft copolymers by precipitation methods would be attributed to the application of this principle. If a θ-solvent is available which has widely different θ-temperatures for the two homopolymers, the modified precipitation technique is very advantageous because solution and precipitation of polymers can be done merely by raising and lowering the solution temperature.

2) Extraction

In the grafting onto fibers or films, the homopolymer occluded in the grafting product is conventionally removed by extraction with a selective solvent(13). This method is in itself relatively

simple and hence most widely used, though often time-consuming. However, it is pointed out that a relatively appreciable amount of homopolymer can be furthermore extracted if the unreacted substrate polymer has been previously removed. According to Stannett and collaborators(2), the conventional extraction method is inadequate to obtain the pure graft copolymer free of homopolymers, unless both homopolymers are subjected to a repeated, alternate extraction. We have also revealed in the previous chapters that the alternate extraction is necessary for the separation of various grafting products. During those experiments several problems arose with respect to the extractability of homopolymers.

First we will examine the possibility whether the graft copolymer is also "dissolved" away as micelle into the extracting solvent. If this actually occurs, the extraction method cannot be applied.

2-1) Dispersibility of graft copolymers into selective solvents

Because a graft copolymer has in the same molecule two sequences different in their solubility behavior, it seems possible that graft copolymer is dispersed into the extracting solvent, resulting in micelle formation. In fact Kotaka et al.(14) and Uchida et al.(15) observed that A-B type block copolymers could pass spontaneously from a dried state into a dispersion when immersed in their selective solvents.

We studied the dispersibility of several pure PVAC-styrene graft copolymers with one PS branch into various selective solvents mainly at room temperature. The experiment was done with two kinds of the dried samples; one was recovered from tetrahydrofuran solution by pouring it into water and the other from the benzene solution into n-hexane. The former was named sample A and the latter sample B. From the difference in interaction of each polymer sequence with those solvents, sample A is supposed to have approximately such a microstructure that PVAC chains are extended and PS chains collapsed, while sample B has the inverse structure. A similar tendency was pointed out also by Merrett(16). The results are summarized in Table 6-3.

It is obvious from the table that neither sample A or B could be dispersed in the solvents in which one chain is soluble but the

Table 6-3. Dispersibility of PVAC-styrene graft copolymers into various solvents from the dried samples at room temperature; graft copolymer/solvent = 1/100 (w/v).

Solvent	PVAC[1]	PS[2]	M3S		M8S		M9S		M10S	
			A	B	A	B	A	B	A	B
Methanol	soluble	insoluble	ND	ND	ND	ND	ND	ND	ND	ND
CH[3]	insoluble	T_θ=34°C	ND	ND	ND	ND	ND	ND	ND	ND
Acetone	soluble	swollen	D	D	D	D	D	D	PD	PD
EAA[4]	soluble	T_θ=108.5°C	D	D	D	D	D	D	D	ND
OAc[5]	T_p=83°C[6]	soluble	ND	D	ND	D	ND	D	ND	PD

A: graft copolymer recovered by pouring the dilute THF solution into water.

B: graft copolymer recovered by pouring the dilute benzene solution into n-hexane.

D: dispersed, PD: partially dispersed, ND: not dispersed.

1) $\overline{M}_n$= 1.14 x 10^5, 2) $\overline{M}_n$= 2.11 x 10^5, 3) cyclohexane (at 50°C), 4) ethyl acetoacetate, 5) n-octyl acetate, 6) initial cloud point.

other is completely insoluble (methanol and cyclohexane). On the other hand, in the solvent which can swell the insoluble chain to a significant extent (acetone), both samples A and B could be completely dispersed and the solution appeared opalescent by reflected light. A similar appearance was observed in ethyl acetoacetate and n-octyl acetate which are θ-solvents for less soluble chains and good solvents for the other. However, in n-octyl acetate sample A was hardly dispersed, though sample B was completely dispersed. Since n-octyl acetate is a selective solvent similar to ethyl acetoacetate except that the PS branch is soluble in the former while the PVAC backbone is soluble in the latter, it cannot be ignored that the sequential structure of the graft copoly-

mer influences its dispersibility in these θ-solvents. Anyway, if one of the component polymers is quite insoluble in the selective solvent, it is clear that the dispersion does not occur, regardless of the sequential structure of the graft copolymer molecule and the microstructure of its bulk sample. The reason that such specific behavior was not observed distinctly for M10S may be due to its higher molecular weight.

As a conclusion one can say that the graft copolymer with at least one branch can be isolated by the extraction method with the selective solvent which is a good solvent for the one chain, but a fully bad solvent for the other. Even if dispersion into the extracting solvent occurred as frequently observed in the isolation of the graft copolymers with numerous branches(17) or A-B type block copolymers(14), they might be freed from the homopolymers by decreasing the solvency of extracting solvent for the soluble chain, for example, by adding a precipitant for the both homopolymers till the copolymer micelle is coagulated.

2-2) Factors affecting the extractability

In contrast with mechanically-blended homopolymers, grafting products need to be extracted alternately with each selective solvent and besides for a very long period. Fig. 6-2 shows a typical example of the alternate extraction for the product obtained by radiation grafting of MMA onto PVA films. The numbers in the figure denote the order of the extraction. As is obviously seen, it is essetial for the effective removal of the homopolymers to repeat the alternate extraction several times. Since the molecular weight of the PMMA homopolymer was so high as several million in this case, employment of better extracting solvents than acetone and water, such as benzene and water - n-propanol (75 : 25) mixture, was further required for the effective extraction. For the sample consisting of PMMA of the average molecular weight ($\overline{M}_n = 1.8 \times 10^5$) comparable to that of PVA the extraction was more complicated as shown in Chapter 3; the extract solution for PVA became milky and the separation into two phases did not occur even by centrifugation. This means that the PVA-MMA graft copolymer whose branch has the length comparable to that of the backbone

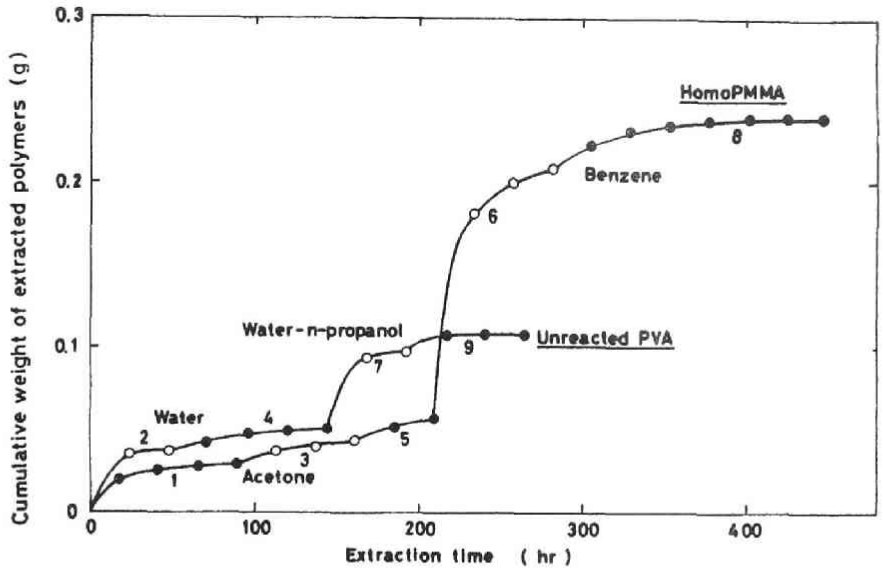


Fig. 6-2. Alternate extraction of PMMA homopolymer and unreacted PVA from the reaction product obtained by the mutual irradiation grafting of MMA onto water-swollen PVA films.

can be dispersed as micelle into water - n-propanol. Therefore, in this case water was used instead of water - n-propanol mixture as the solvent to extract the unreacted PVA.

On the other hand, the similar alternate extraction gave an erroneous result for the reaction product (M9S) obtained by the grafting of styrene onto PVA (extractions 1-7 in Fig. 6-3), unless the PVA part in the product was acetylated to PVAC. The acetylation was carried out for the residue taken out in the middle stage of the 2nd extraction (at A in Fig. 6-3) and the PVAC and PS were extracted with methanol and cyclohexane, respectively. The result is also given in Fig. 6-3 (broken line). As can be seen, the acetylation enabled us to remove the homopolymers successfully. The removal of the homopolymers from the unacetylated reaction product appears to be accomplished at the 7th extraction, but extraction 3' for the acetylated sample indicates that the unreacted PVA remained unextracted still in the 7th extraction residue by such an amount as nearly equal to that of the PVA component in the graft

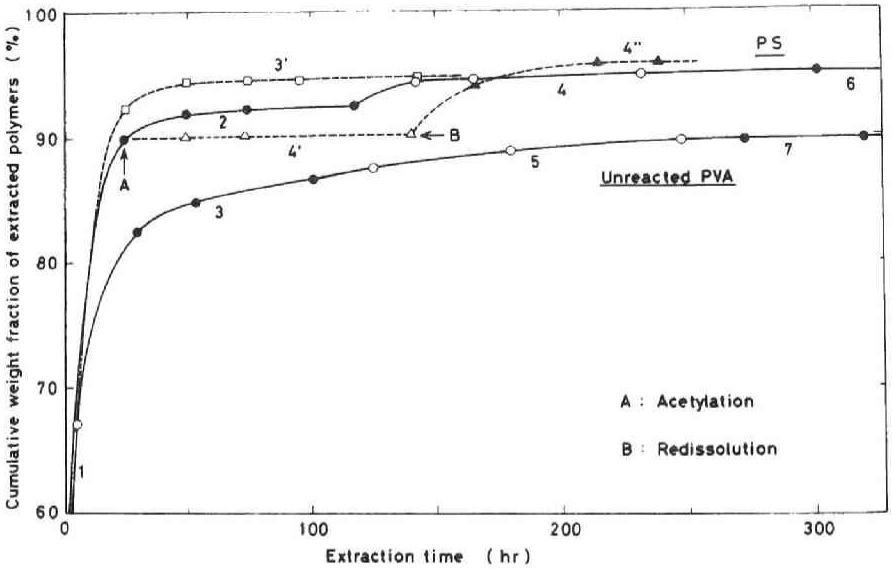


Fig. 6-3. Alternate extraction of PS homopolymer and unreacted PVA (or acetylated) from the reaction product (M9S) obtained by the mutual irradiation grafting of styrene onto water-swollen PVA films.(The weight of extracted PVAC was plotted in this figure as that of PVA.)

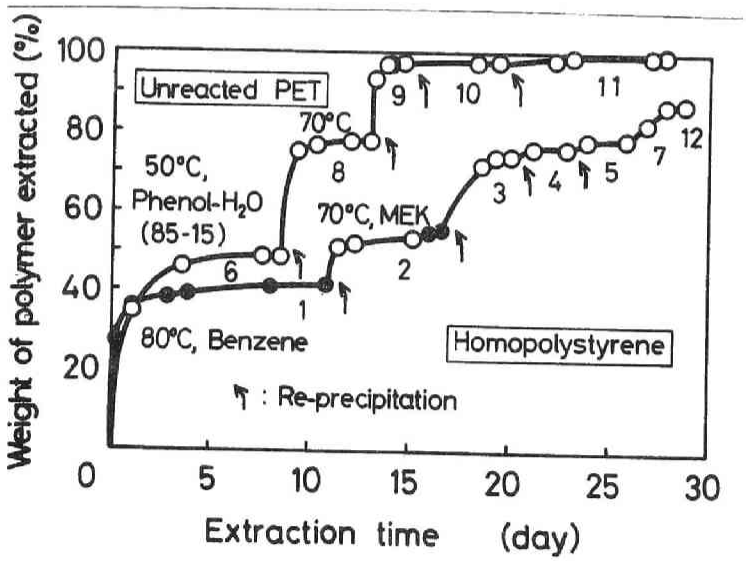


Fig. 6-4. Extraction of PS homopolymer and unreacted PET from the reaction product obtained by the preirradiation grafting of styrene onto PET fibers.

copolymer. Further discussion on this figure will be given later.

A similarly poor efficiency extraction can be seen also in Fig. 6-4, where the extraction result for the product obtained by the radiation grafting of styrene onto poly(ethylene terephthalate) (PET) fibers(18) is shown. In this case the unreacted PET was extracted after most of PS homopolymer was extracted by repeated solution-precipitation of the sample. It should be mentioned here that the solution procedure was also necessary to achieve the extraction of the unreacted PET, though most of PS homopolymer had been already removed. Also for nylon-styrene(18) and poly(vinyl chloride)-acrylonitrile(19) grafting products, such solution-precipitation procedure was necessary to remove the homopolymers to a sufficient extent.

The difficulties in the above-mentioned extraction may be chiefly attributed to the microstructure of the sample to be extracted, because the rate of extraction may depend on whether the polymer molecule to be extracted is extented, or collapses in the outer component phase(20). In the experiment shown in Fig. 6-3, PS was attempted to be extracted from the acetylated sample with cyclohexane at 50 ^{o}C, after the PVAC homopolymer was removed. However, the PS homopolymer could hardly be extracted as shown by curve 4'. Since this sample was recovered by pouring the acetylation mixture, i.e., the pyridine - acetic anhydride solution into cold water, it may have such a microstructure as the PS chain is collapses and is occluded in the continuous phase of the extended PVAC. Therefore, to invert the microstructure of the sample it was again dissolved in tetrahydrofuran and recovered by pouring the solution into n-hexane whose nonsolvency is much stronger for PVAC than PS (at B in Fig. 6-3). Then extraction was carried out with cyclohexane at 50 ^{o}C. The result is shown by curve 4'' in Fig. 6-3. It is clear that the extended PS homopolymer could be readily removed by this further extraction, as expected.

Thus for the successful removal of homopolymers it is evidently necessary to take into consideration the microstructure. When we change the microstructure by the solution-precipitation, this may additionally destroy the crystallite or the intimate entanglement among polymer molecules making the extraction difficult.

3) Adsorption chromatography

The isolation of graft and block copolymers by a chromatographic technique has been reported not so extensively. Also in this case, the emulsifying effects should be considered. Recently, it has been reported that thin-layer chromatography is very useful to fractionate polymer mixtures(21-25). Thus we applied a column adsorption chromatography for the isolation in order to find its more rapid and simple method than selective precipitation or extraction.

The sample used in the present work is the product prepared under the same condition as Sample M9S. Prior to chromatographic separation, it was subjected to rough extraction of unreacted PVA and PS homopolymers. The PVA part in the product was completely acetylated to PVAC. Silica gel (100 mesh) from Mallinckrodt Chemical Works, U.S.A., was washed with water to remove free acid, rinsed with methanol, and dried at 100-105°C for 15 hrs. Then it was charged by a wet method with benzene to a column of 50-cm height and 2.2-cm diam equipped with a glass jacket. Water was circulated in the clearance at 25°C from a thermostat. After washing the column with benzene, the polymer solution (308.0 mg/30 ml benzene) was allowed to flow. The rate flow was kept 0.3-0.4 ml/min throughout the experiment.

The solvents used as eluent are benzene for PS, methanol for PVAC, and methyl ethyl ketone (MEK) for the graft copolymer. Evidently, the separations with benzene and MEK are based on the difference in adsorption strength of the polymers to silica gel, whereas that with methanol on the difference in the solubility of the polymers for the solvent. In order to avoid mixing of benzene and methanol, carbon tetrachloride (CCl_4), with which any of three polymers are not at all eluted, was allowed to run between the elutions with benzene and methanol. Each solvent was made to flow till the amount of eluted polymer became negligible, and then replaced by the subsequent solvent.

Fig. 6-5 shows the chromatogram where the polymer concentration c is plotted against the elution volume. It seems that the product is expectedly divided into three fractions by this chromatography. However, in order to confirm whether the chromato-

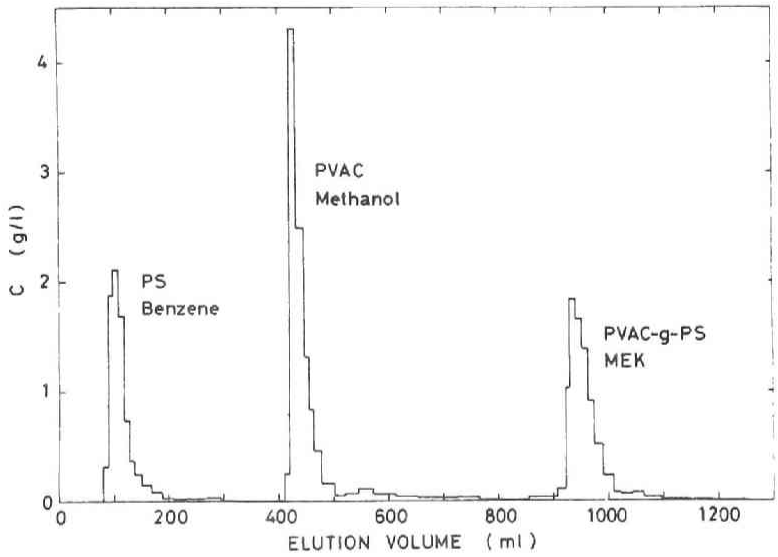


Fig. 6-5. Chromatogram of grafting reaction product using successively benzene, methanol, and MEK as eluent.

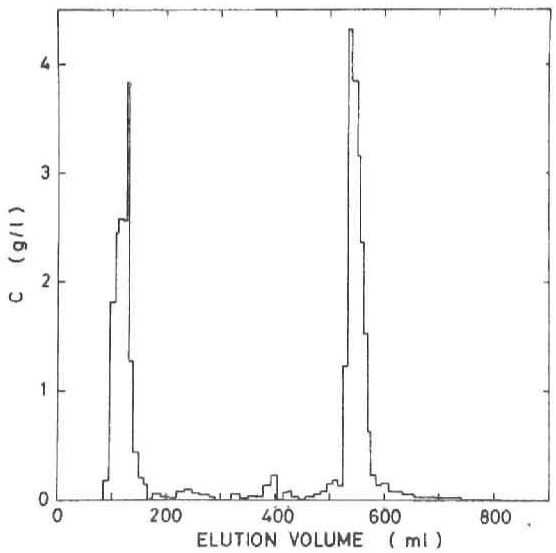


Fig. 6-6. Chromatogram of PS/PVAC/PVAC-g-PS mixture using mixed solvent as eluent.

graphic separation is really effective, it is necessary to determine the extent of contamination of the three fractions. Thin-layer chromatographic analysis, which is discussed later, for the fractions of the graft copolymer indicates that each fraction is not contaminated with either homopolymer by more than 0.5-1 wt%. This contamination could be decreased if the elutions would be continued further with respective solvents. It was found from IR spectra that PS fractions were not virtually contaminated with PVAC, while initial PVAC fractions contained PS component to a larger than negligible amount. This may be due to the elution of a small amount of the graft copolymer with CCl_4-methanol mixture formed during the replacement of CCl_4 by methanol. The recovery of the polymers was quite quantitative (308.0 mg used, 308.6 mg recovered), but partial hydrolysis took place when removal of free acid from the silica gel was insufficient.

On the other hand, when the separation was performed based only on the difference in the adsorption behavior, the PVAC-styrene graft copolymer could not be separated from PVAC homopolymer. The result is given in Fig. 6-6. The sample is blend of PS(100mg), PVAC(100mg), and PVAC-styrene graft copolymer(100 mg) isolated by extraction method. PS was eluted at first with benzene as thoroughly as possible. Then the concentration gradient elution was further continued by using benzene- methyl acetate mixture as a eluent. Elution characteristics of methyl acetate is similar to that of MEK for the polymers. From Fig. 6-6 it seems likely that PVAC and the graft copolymer were eluted at the same time though the chemical composition of the two polymers is widely different from each other.

In conclusion, we can say that the reaction product can be successfully and rapidly separated into its three components if the elution condition is properly chosen.

ESTIMATION OF THE PURITY OF GRAFT COPOLYMERS

Ende and Stannett(9) first applied the density gradient centrifugation method to a graft copolymer to check if the given sample was free from one or both of the attendant homopolymers.

However, the technique has scarcely been used in the field of graft copolymers in spite of the lack of other suitable methods, probably because the choise of solvent pairs to produse a suitable density gradient is quite difficult. Clearly, the turbidimetric titration method is not appropriate to detect the homopolymer contaminating by a relatively small amount. On the other hand, thin-layer chromatography (tlc) appears to be a feasible technique. Recently it has been reported that the tlc technique makes possible to fractionate polymers through the differences in composition(21, 21), monomer arrangement(23), steric isomerism(24,25), and molecular weight(26-30). Especially Inagaki et al.(23) observed that block copolymers were not developed on a chromatoplate, though the corresponding homopolymers, statistical and alternate copolymers had a high R_f-value. Thus it seems highly possible by tlc to check the purity of graft copolymers.

The chromatographic behavior of a polymer in adsorption chromatography is known to depend on the polarity of solvent and polymer and the activity of stationary phase (especially in tlc). For instance the more polar a solvent the more possible it is for the polymer to be developed. In the case of mixture of poly-A and poly-B (say, poly-A is less polar than poly-B), merely poly-A would be developed, if suitable solvent is used as a developer. On the contrary, it is impossible to develop solely the more polar poly-B as far as tlc proceeds via the adsorption-desorption mechanism. In this case we must use such a developer that allows the development to take place by a selective elution mechanism. For this purpose the solvent should be highly polar, and a good solvent for poly-B but a bad solvent for poly-A.

The tlc substrate used in the present study were silica gel with a thickness of 0.25 mm precoated on 5 x 20 cm or 20 x 20 cm glass plates (Merck A.G., Darmstadt, Germany). The polymer (4-40μg) was deposited as a band of 5 cm length parallel to the developing direction using a microsyringe. The band-like deposition was made because about 40μg was necessary to determine so small an amount of homopolymer occluded in the sample and such a large amount of polymer could not be normally developed when deposited as a spot. Some developers used are tabulated in Table 6-4

Table 6-4. Experimental conditions of thin-layer chromatography for graft copolymers

Sample	Spotting solvent	Homopolymer		Mother polymer	
		Developer	Indicator	Developer	Indicator
CTA-g-PS	$CHCl_3$	$CHCl_3$	$HClO_4$ 10 % aq.	CH_2Cl_2/CH_3OH = 1/1	$HClO_4$ 10 % aq.
PVAC-g-PS	$CHCl_3$	$CHCl_3$	$HClO_4$ 10 % aq.	CH_3OH/H_2O = 9/1[a]	$HClO_4$ 10 % aq.
PVAC-g-PMMA	$CHCl_3$	MEK/CCl_4 = 8/2	I_2 N/20 aq.	CH_3OH/H_2O = 9/1[a]	I_2 N/20 aq.
Nylon-g-PS	HCOOH/$CHCl_3$ = 2/8	$CHCl_3$	$HClO_4$ 10 % aq.	HCOOH[a]	I_2 N/20 aq.
PET-g-PS	Phenol/CH_3OH = 95/5	$CHCl_3$	Kayalon Fast Brown R[b] H_2O-CH_3OH soln.	Phenol/H_2O = 75/25	Kayalon Fast Brown R[b] H_2O-CH_3OH soln.

a) continuous development.

b) manufactured by Nippon Kayaku Co.,Ltd.

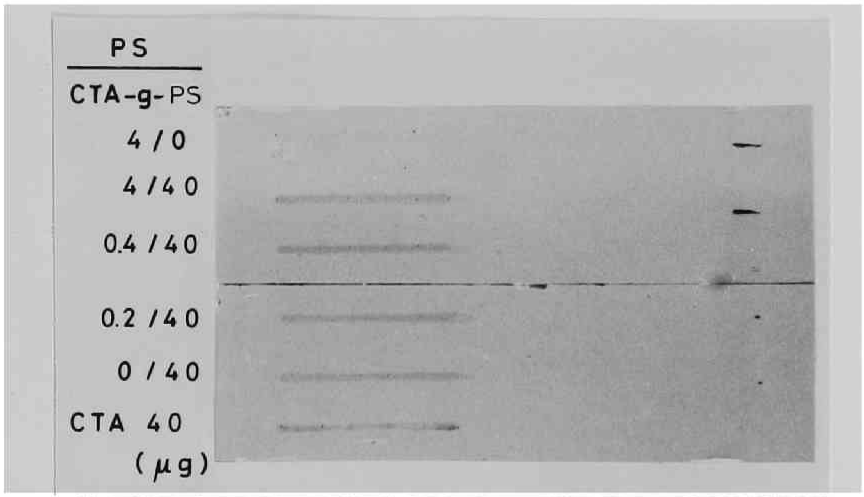


Fig. 6-7. Thin-layer chromatograms of the PS homopolymer, the CTA homopolymer, the isolated CTA-g-PS, and the PS - CTA-g-PS mixtures with different mixing ratios (developer : chloroform).

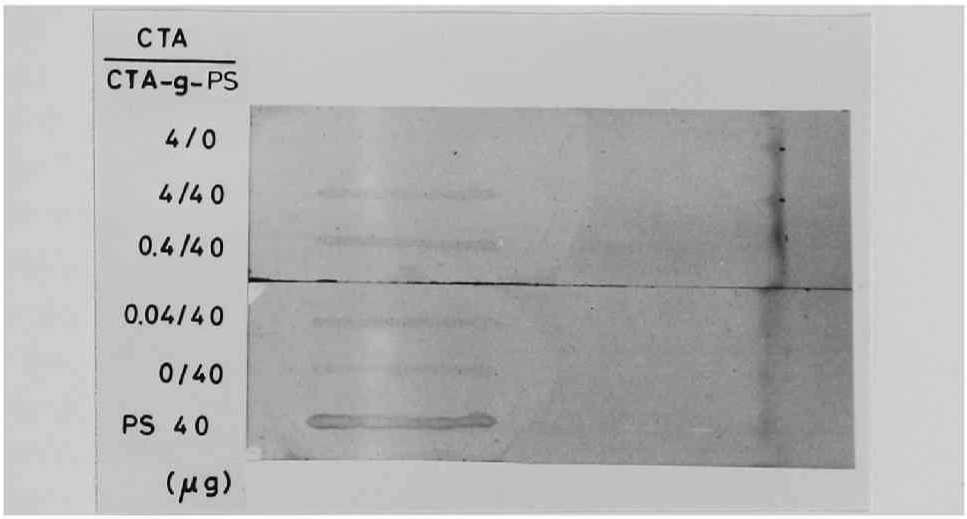


Fig. 6-8. Thin-layer chromatograms of the CTA homopolymer, the PS homopolymer, the isolated CTA-g-PS, and the CTA - CTA-g-PS mixtures with different mixing ratios (developer: methanol-methylene chloride(1 : 1) mixture).

togather with solvents for preparing sample stock solutions and indicators used for staining of chromatograms. All of the samples are the graft copolymers prepared by radiation graftings and subjected to the isolation by either of the above-mentioned methods. In any case tlc was carried out not only for the graft copolymer sample, but also for the mixtures of the sample and the homopolymer of a given amount in order to estimate quanti-

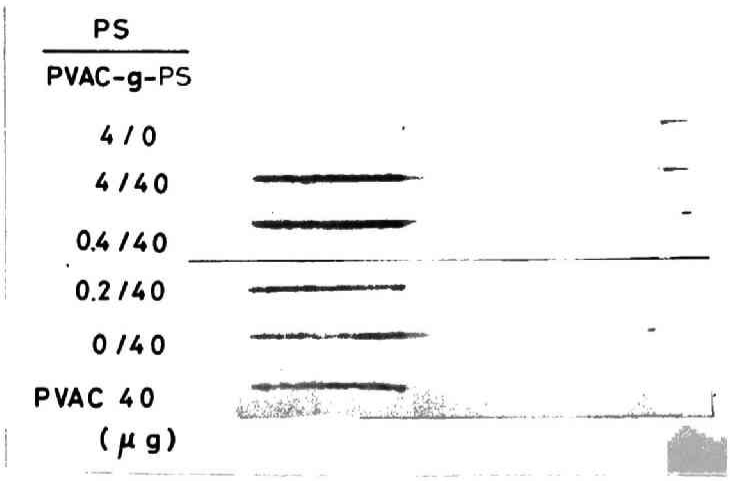


Fig. 6-9. Thin-layer chromatograms of the PS homopolymer, the PVAC homopolymer, the isolated PVAC-g-PS(M9S), and the PS - PVAC-g-PS mixtures with different mixing ratios (developer: chloroform).

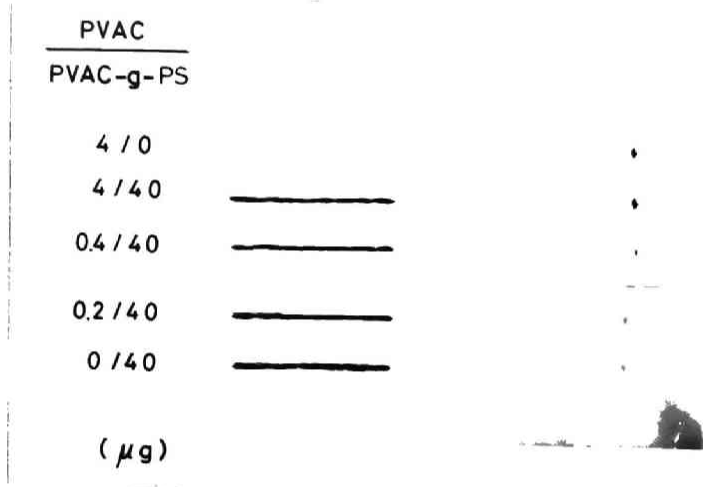


Fig. 6-10. Thin-layer chromatograms of the PVAC homopolymer, ~~the PS homopolymer,~~ the isolated PVAC-g-PS(M9S), and the PVAC - PVAC-g-PS mixtures with different mixing ratios (developer: methanol-water (9 : 1) mixture).

tatively the amount of the attendant homopolymer.

Figs. 6-7, 6-8, 6-9, and 6-10 show typical chromatograms of cellulose triacetate-g-PS and PVAC-g-PS(M9S). The scanning spectrodensitometric traces for PS in the chromatogram of PS - PVAC-g-PS mixtures by the reflected light of 265 nm are given in Fig. 6-11. Other graft copolymers gave similarly clear chromatograms..

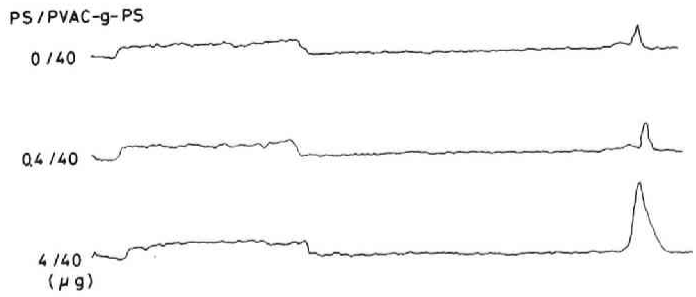


Fig. 6-11. Scanning spectrodensitometric traces for PS in the chromatograms of the PS - PVAC-g-PS (corresponding to Fig. 6-9).

It is probable from these results that the graft copolymers are not developed, the corresponding homopolymers alone being developed, as reported by Inagaki et al.(23) In these studies we could detect the homopolymers contaminating by amounts of 0.5 - 1.0 %, though the development with the selective solvents had to be continued overnight in several cases by the continuous development method(31).

From the comparison of the staining degree of developed polymers in tlc for the mixtures of graft copolymer and its homopolymer, the purity of the cellulose-g-PS was found to be above 99 %. Those of PVAC-g-PS (M3S, M8S, M9S, and M10S) and nylon-g-PS were 95 -98 %. On the other hand, the PVAC-g-PMMA and PET-g-PS were, in some cases, contaminated with their homopolymers of about 10 %. The poor separation of the homopolymers from the PVAC-g-PMMA may be due to the fact that the solution - precipitation was not carried out. The extraction of PS homopolymer from the PET-g-PS sample might be not sufficiently effective since the adequate inversion of microphase would not be attained by the solution - precipitation.

REFERENCES

1) F. M. Merrett, Trans. Faraday Soc., 50, 759 (1954).
2) H. Yasuda, J. A. Wrag, and V. Stannett, J. Polym. Sci., C, 2, 387 (1963).

3) E. E. Magat, I. K. Miller, D. Tanner, and J. Zimmerman, J. Polym. Sci., C, 4, 615 (1963).
4) H. Sumitomo, S. Takakura, and Y. Hachihama, J. Chem. Soc. Japan, Ind. Chem. Sec. Kogyo Kagaku Zasshi , 66, 269 (1963).
5) I. Sakurada, S. Matsuzawa, and Y. Kubota, Makromol. Chem., 69, 115 (1963).
6) I. Sakurada, Y. Ikada, and Y. Uesaki, Bull. Inst. Chem. Res., Kyoto Univ., 47, 49 (1969).
7) I. Sakurada, Y. Ikada, and F. Horii, Bull. Inst. Chem. Res., Kyoto Univ., 47, 58 (1969).
8) C. J. Hamburger, J. Polym. Sci., A-1, 7, 1023 (1969).
9) H. A. Ende and V. Stannett, J. Polym. Sci., A, 2, 4047 (1964).
10) Chapter 9
11) G. E. Molau, in Characterization of Macromolecular Structure, D. McIntire, Ed., National Academy of Science, Washington, D. C., 1968, Chapter 3.
12) I. Sakurada, Y. Ikada, and Y. Nishizaki, J. Polym. Sci., C, 37, 265 (1972).
13) H. A. J. Battaerd and G. W. Tregear, Graft Copolymers, Interscience, New York, 1967.
14) T. Kotaka, T. Tanaka, and H. Inagaki, Polym. J., 3, 327 (1972).
15) T. Uchida, T. Soen, T. Inoue, and H. Kawai, J. Polym. Sci., A-2, 10, 101 (1972).
16) F. M. Merrett, J. Polym. Sci., 24, 467 (1957).
17) Y. Ikada, K. Maejima, and I. Sakurada, unpublished work .
18) I. Sakurada, Y. Ikada, and T. Kawahara, J. Polym. Sci., Polym. Chem. Ed., 11, 2329 (1973).
19) Chou Kwang-Fu, Y. Ikada, and I. Sakurada, unpublished work.
20) R. J. Ceresa, Block and Graft Copolymers, Butterworths, London, 1962.
21) H. Inagaki, H. Matsuda, and F. Kamiyama, Macromolecules, 1, 520 (1968).
22) V. G. Belenkii and E. S. Gankina, Dokl. Akad. Nauk. SSSR, 186, 857 (1969).
23) F. Kamiyama, H. Matsuda, and H. Inagaki, Makromol. Chem., 125, 286 (1969).
24) H. Inagaki, T. Miyamoto, and F. Kamiyama, J. Polym. Sci., B,

7, 329 (1969).
25) T. Miyamoto and H. Inagaki, Macromolecules, 2, 554 (1969).
26) H. Inagaki, Bull. Inst. Chem. Res., Kyoto Univ., 47, 196(1969)
27) E. P. Otocka and M. Y. Hellman, Macromolecules, 3, 392 (1970).
28) E. P. Otocka, Macromolecules, 3, 691 (1970).
29) B. G. Belenkii and E. S. Gankina, J. Chromatogr., 53, 3 (1970).
30) F. Kamiyama, H. Matsuda, and H. Inagaki, Polym. J., 1, 518 (1970).
31) J. G. Kirchner, in Techniques of Organic Chemistry, Vol. XII, Thin-Layer Chromatography, E. S. Perry and A. Weissberger, Ed., Interscience, New York, 1967.

CHAPTER 7

EMULSIFYING EFFECT OF GRAFT COPOLYMER FOR THE HOMOPOLYMER

INTRODUCTION

Block and graft copolymers have sequences of different monomer units in a molecule. These copolymers are, therefore, expected to exhibit a number of unique properties which cannot be observed when the corresponding homopolymers are employed. One of these properties may be an emulsifying power as observed with low molecular weight surfactants. For instance, Hughes and Brown(1) found that solutions of a polystyrene-poly(ethyl acrylate) mixture prepared from the product of polymerization of styrene in poly(ethyl acrylate) emulsion apparently consisted of a single, hazy phase, while the physical mixture of these homopolymers separated into two distinct layers when dissolved in common solvents. A similar phenomenon was also reported by Molau in several polymer-polymer systems(2). He concluded that this must be due to emulsifying ability of the graft copolymer which would have been formed during polymerization, and accumulated on the surface of droplets of polymer solution.

Recently Wellons and co-workers(3) found a particularly interesting property of graft copolymer : films cast from solutions of two immiscible homopolymers containing a small amount of the corresponding graft copolymer were transparent, while those prepared from a mixture of homopolymers without copolymer were translucent. This effect of graft or block copolymers was studied more extensively by Riess and co-workers (4 - 6), and it was shown that the incompatibility of two homopolymers could be reduced by addition of block copolymer which acts as an emulsifier.

It has frequently been pointed out (7) that isolation of graft copolymers by means of fractional precipitation technique from a reaction mixture containing two homopolymers corresponding to backbone and branch, is very tedious, since a stable colloidal suspension is readily formed which resists aggregation by most of the common methods. It seems highly plausible that this undesirable stabilization of colloidal solutions

is just a consequence of the above mentioned emulsifying effect of the co-existing graft copolymer.

The purpose of this work is to investigate more or less quantitatively the emulsifying effects of graft copolymers using well-characterized samples. In the present work we will report the effect of graft copolymer on the protection of the corresponding homopolymers against precipitation from the solution caused by addition of the precipitant, resulting in emulsion formation. The graft copolymers used are poly(vinyl alcohol)(PVA) g- methyl methacrylate) and poly(vinyl acetate)-g-methyl methacrylate . They have one grafted branch whose length is approximately equal to that of the backbone. The homopolymer to be protected from precipitation is poly(methyl methacrylate)(PMMA) with various degrees of polymerization. Dimethyl sulfoxide(DMSO) was used as a common solvent, and water as a selective precipitant of PMMA.

A study concerning graft copolymer effects on the emulsion formation in a polymer-polymer-good solvent system will be presented in the following chapter.

EXPERIMENTAL

1. Graft copolymer

The PVA-MMA graft copolymer was prepared by mutual irradiation grafting mentioned in Chapter 4. Each graft copolymer molecule has one branch. The degree of polymerization(DP) of the branch and the backbone were 1,810 and 2,740 for sample M1M, and 1,560 and 2,780 for M7M, respectively. In the present study the sample M1M was used, unless otherwise stated.

2. Homopolymers

HomoPMMA's with DP of 870, 1,040, 1,200, 1,500 and 1,770 were those which were formed during grafting. HomoPMMA with DP of 3,540 was obtained by bulk polymerization with azobisisobutyronitrile as an initiator. The DP was measured in every case

osmometrically and all the samples were used without fractionation.

3. Precipitation equilibrium

The homoPMMA and the graft copolymer were dissolved at the same time in DMSO in test tubes, the concentration of homoPMMA being always maintained at 1.0 % and that of the graft copolymer being varied widely. A known amount of water was added to the solution at room temperature and the tube was sealed. The sealed tube was then heated on a boiling water bath to redissolve the polymer which had been precipitated by the addition of water. After complete dissolution, the tube was put in a thermostat at 30°C for 48hr to equilibriate the precipitation or the liquid-liquid phase separation. The equilibrium was generally reached within a day.

The polymer precipitated to equilibrium was isolated from the solution by decantation (in an exceptional case centrifugation was applied), washed with methanol or water, dried and weighed. In the case of phase separation, the higher concentrated phase was separated from the less concentrated upper liquid phase by decantation and the polmer was recovered by addition of methanol or water.

4. Electron microscopy

Electron microscopic photographs were taken after colloidal suspensions containing homoPMMA protected from precipitation were dialyzed against water to exchange DMSO for water and condensed to dryness on collodion or poly(vinyl formal) film at room temperature. For comparison an electron microphotograph was taken after the same suspension was coagulated by pouring into methanol, dried and then again dispersed on collodion film.

RESULTS

1. Influence of graft copolymer and water concentrations on the precipitation of homoPMMA

In the present work the emulsifying effect of the graft co-

polymer was studied under the condition that the homopolymer is precipitated, while the graft copolymer is still held in the solution. The solvent-precipitant combination adopted here was DMSO-water. The concentration of homoPMMA in DMSO was kept at 1.0 % and various amounts of the precipitant (H_2O) were added.

Fig. 7-1 shows the precipitation curve of homoPMMA in DMSO-water mixture at 30°C.

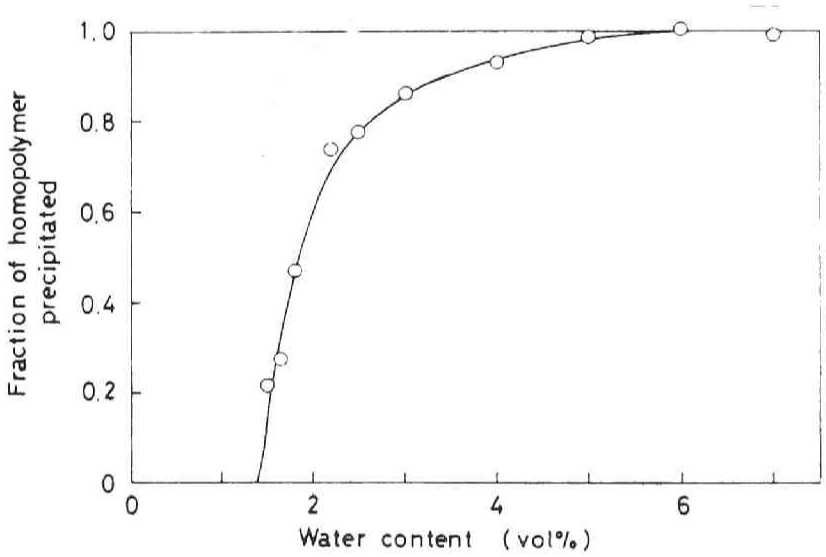


Fig. 7-1. A precipitation curve of homoPMMA in DMSO-water mixtures (initial polymer conc. = 1.0 wt%, DP = 1,500, temp. = 30°C).

As is seen, the amount of water required to cause precipitation of all the PMMA is very small. The graft copolymer was not precipitated at all by addition of such a small amount of water. The influence of the added graft copolymer on the incipient cloud point of homoPMMA is shown in Fig. 7-2.

The presence of graft copolymer does not affect the cloud points of the solution of homoPMMA, indicating that initial aggregation of homopolymer molecules was not disturbed with the existing graft copolymer, at least by such a small amount of graft copolymer. However, amounts of the homoPMMA precipitated at the bottom of tube were decreased distinctly, when the graft copoly-

mer was present in the solution. The appearance of the solution changed in the following fashion.

When the graft copolymer was absent, the DMSO solution of PMMA became hazy upon addition of water, and then separated into two clear layers within one day. In case that the amount of added water was sufficient enough, the upper phase contained practically no polymer, while the lower phase consisted of swollen, precipitated homoPMMA. This is quite the well-known phenomenon observed with ordinary solutions of homopolymers. However, when the graft copolymer was present in the solution, the appearance of the upper phase changed from clear to turbid and the amount of homopolymer precipitated at the bottom was decreased and finally became zero with increasing amount of the added graft copolymer.

A typical result is given in Fig. 7-3.
The amount of water was adjusted so as to precipitate the homoPMMA just to completion when the graft copolymer was not added. It can be clearly seen that the precipitation of homoPMMA was greatly reduced by the presence of the graft copolymer. In other words, one can say that the homopolymer was emulsified by the graft copolymer. The minimun amount of the graft copolymer to be added to cause the precipitated polymer phase to disappear was as small as 1.0 % of homoPMMA. In this case the solution became turbid on the whole and this trend was kept unchanged at least for six months. Even if the turbid solution was subjected to centrifugation at 24,300 g for 10 min., a considerable amount of homoPMMA was still held in dispersion without precipitation. The result is given also in Fig. 7-3.

DP of the homoPMMA used in the above experiment was 1,040. The following studies were carried out to see the effect of the DP of homoPMMA on its emulsification and the results are given in Fig. 7-4.
The precipitated polymer was separated by decantation. As is obvious from Fig. 7-4, the emulsifying effect of graft copolymer for the homopolymer became more prominent as the DP of homoPMMA decreased. The similar large dependence of DP of homopolymer

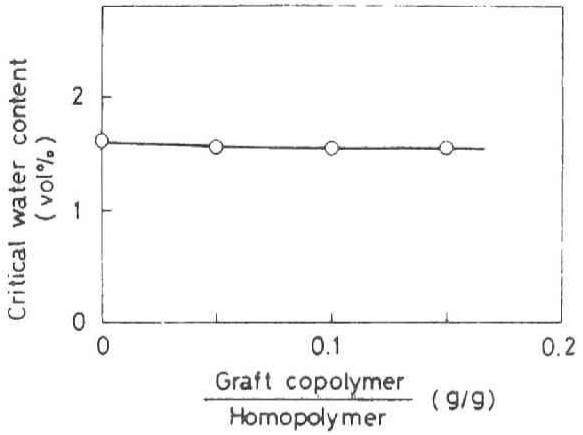


Fig. 7-2. Influence of PVA-MMA graft copolymer on the critical water content necessary for the incipient cloud point of homoPMMA in DMSO-water mixtures (conc. of homopolymer = 1.0 wt%, DP = 1,500).

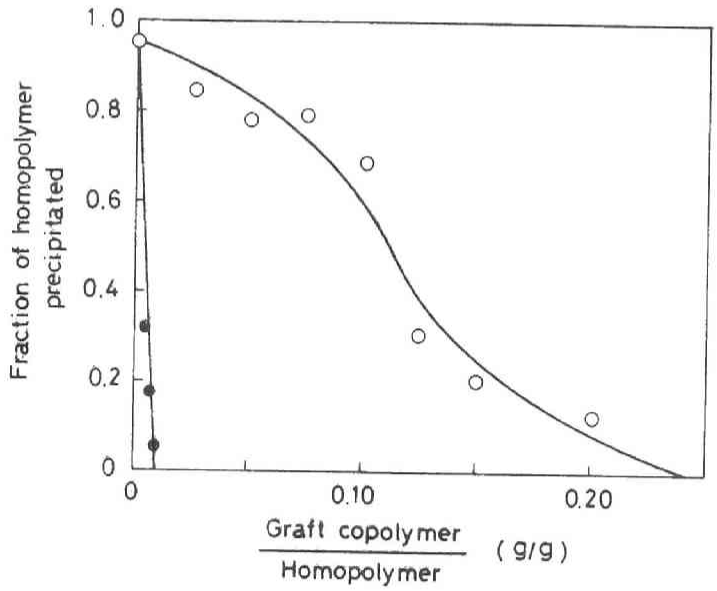


Fig. 7-3. An example of the protection effect of PVA-MMA graft copolymer on the precipitation of homoPMMA. The polymer precipitated was separated by simple decantation (●) or under centrifugation (○). (DP = 1,040).

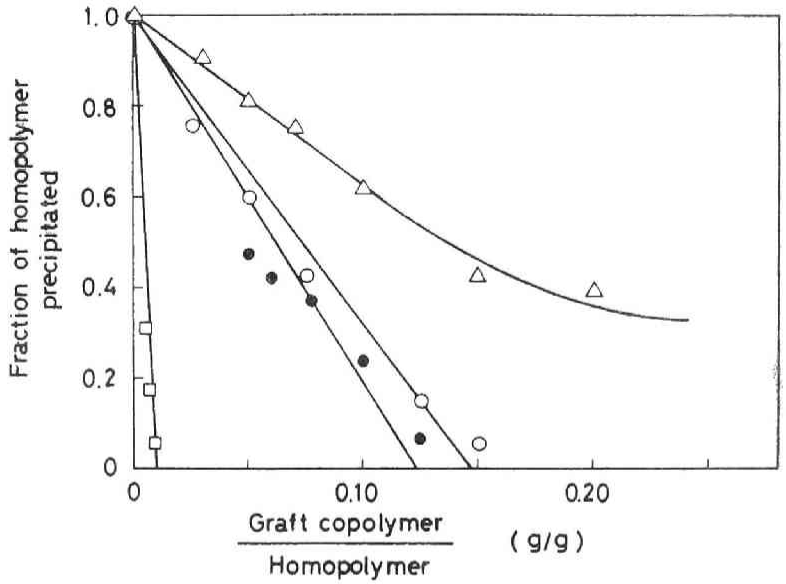


Fig. 7-4. The protection effect of PVA-MMA graft copolymer on the precipitation of homoPMMA with various DP's.

□ : DP = 1,040, water content = 5.0 vol%
● : " = 1,500, " = 6.0 "
○ : " = 1,700, " = 4.0 "
△ : " = 3,540, " = 3.5 "

has been also reported by other workers in the study of compatibilization or solubilization effects of block copolymers on immiscible homopolymers (4 - 6, 8, 9).

In the above experiments a critical amount of water was added which was required to just cause all homopolymers to be precipitated when the graft copolymer was absent. Fig. 7-5 shows the results obtained at experiments whereby the water was added to a smaller extent than the critical amount.
It is seen that a plateau region appeared in the precipitation curves in this case. The upper solution layer was always clear in this concentration range of the graft copolymer, suggesting that the graft copolymer did not influence the phase-separation of homoPMMA solutions. However, when the amount of graft copolymer became higher than a certain threshold value, the emulsification took place, which led to a change in the appearance

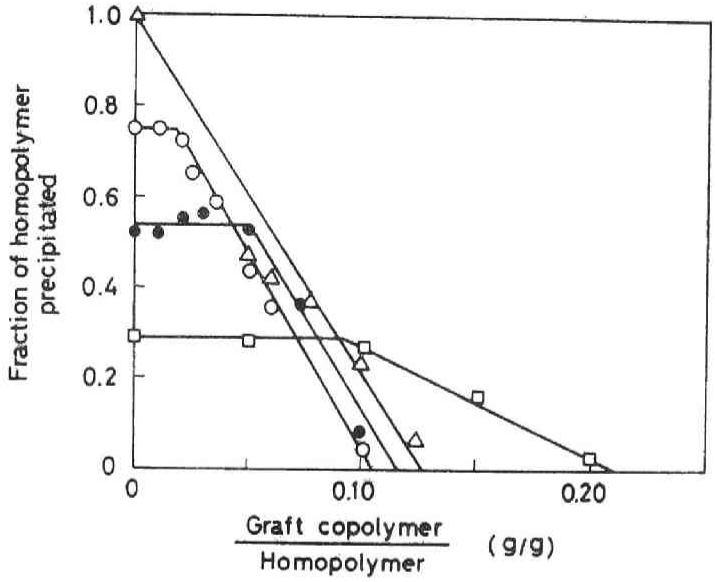


Fig. 7-5. Influence of the water content added by smaller amounts than to cause just total homopolymer to precipitate (DP = 1,500).

□ : water content = 1.6 vol%
● : " = 1.8 "
○ : " = 2.3 "
△ : " = 6.0 "

of the solution phase from clear to turbid.

On the contrary, the result given in Fig. 7-6 was obtained, when a larger amount of water was added than the critical amount. In this case, the precipitation of homopolymer could be prevented by a smaller amount of the graft copolymer, as long as the added amount was small.

From the results given in Figs. 7-5 and 7-6, we can draw a phase diagram for emulsification of the homopolymer as functions of the graft copolymer and the precipitant (water) contents. This is represented in Fig. 7-7, where open circles correspond to the graft copolymer content at the end of the plateau region in Fig. 7-5 and filled circles to those by which all the homopolymer is just emulsified, as shown in Figs. 7-5 and 7-6. In the region I the added graft copolymer does not influence the precipitation of the homopolymer, while it protects the homopoly-

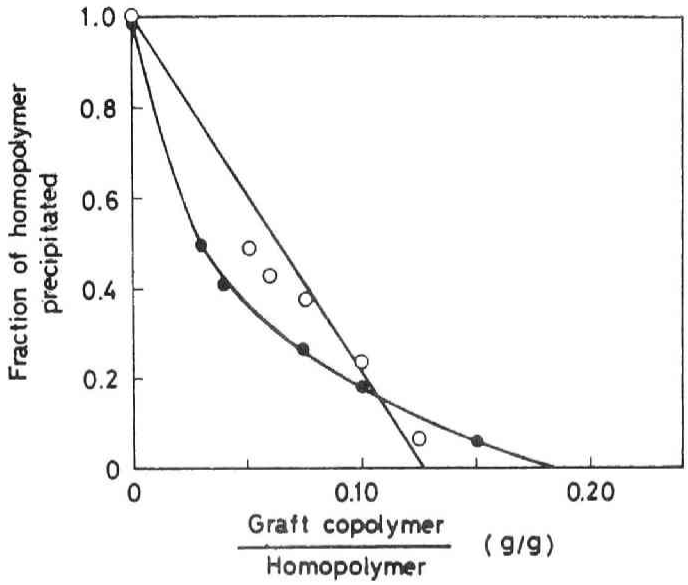


Fig. 7-6. Influence of the water content added by larger amounts than to cause just total homopolymer to precipitate (DP = 1,500).
○ : water content = 6.0 vol%
● : " = 8.0 "

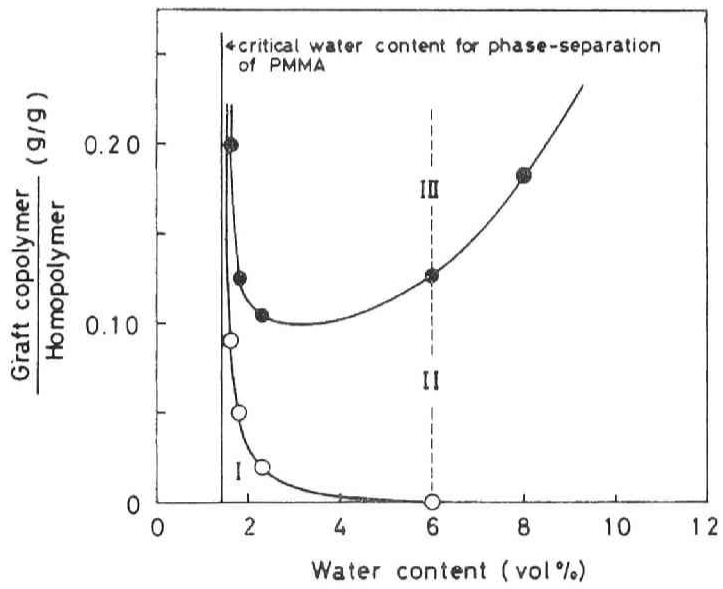


Fig. 7-7. Phase diagram for emulsification of homoPMMA by PVA-MMA graft copolymer in DMSO-H_2O (DP = 1,500). See the text about the symbols in the figure.

mer from precipitation in the region II, though not completely. However, in the region III the homopolymer to be precipitated is thoroughly emulsified by the graft copolymer. The broken line in the figure denotes the critical water content where just total homopolymer would be precipitated in the absence of the graft copolymer. The strong dependence of the water content on the emulsification may be compared with the similar dependence of polymer blend concentration on the polymeric oil-in-oil emulsion formation as will be shown in Chapter 8. It is well known that the phase separation caused by addition of the precipitant (aggregation) proceeds more predominantly with increasing amount of the precipitant, while in the case of blend solutions prepared with a common solvent the tendency of phase-separation (demixing) increases with the blend concentration.

2. Size of emulsion particles

Fig. 7-8 (a) gives a representative electron microphotograph of emulsion taken after subjecting to dialysis against water. One can clearly see round particles which are similar to ordinary emulsion particles. It is interesting to point out that the spherical structure of the particles is apparently preserved even after coagulation of emulsion, as seen in Fig. 7-8 (b), which was taken after the same suspension sample as used for Fig. 7-8 (a) was coagulated by pouring into methanol and pulverized again mechanically.

The particle radius was read from the electron microphotograph and the average radius $\bar{R}$ defined as $\sum_i n_i R_i^3 / \sum_i n_i R_i^2$ was calculated. (The reason for this averaging will be discussed later.)

Table 7-1 lists the average radius of emulsion particles whose photographs were taken after dialysis. The emulsions were prepared by adding the M7M graft copolymer sample by larger amounts than necessary to protect just all the homopolymer. The water content was adjusted to such an amount that all the homopolymer was just precipitated.

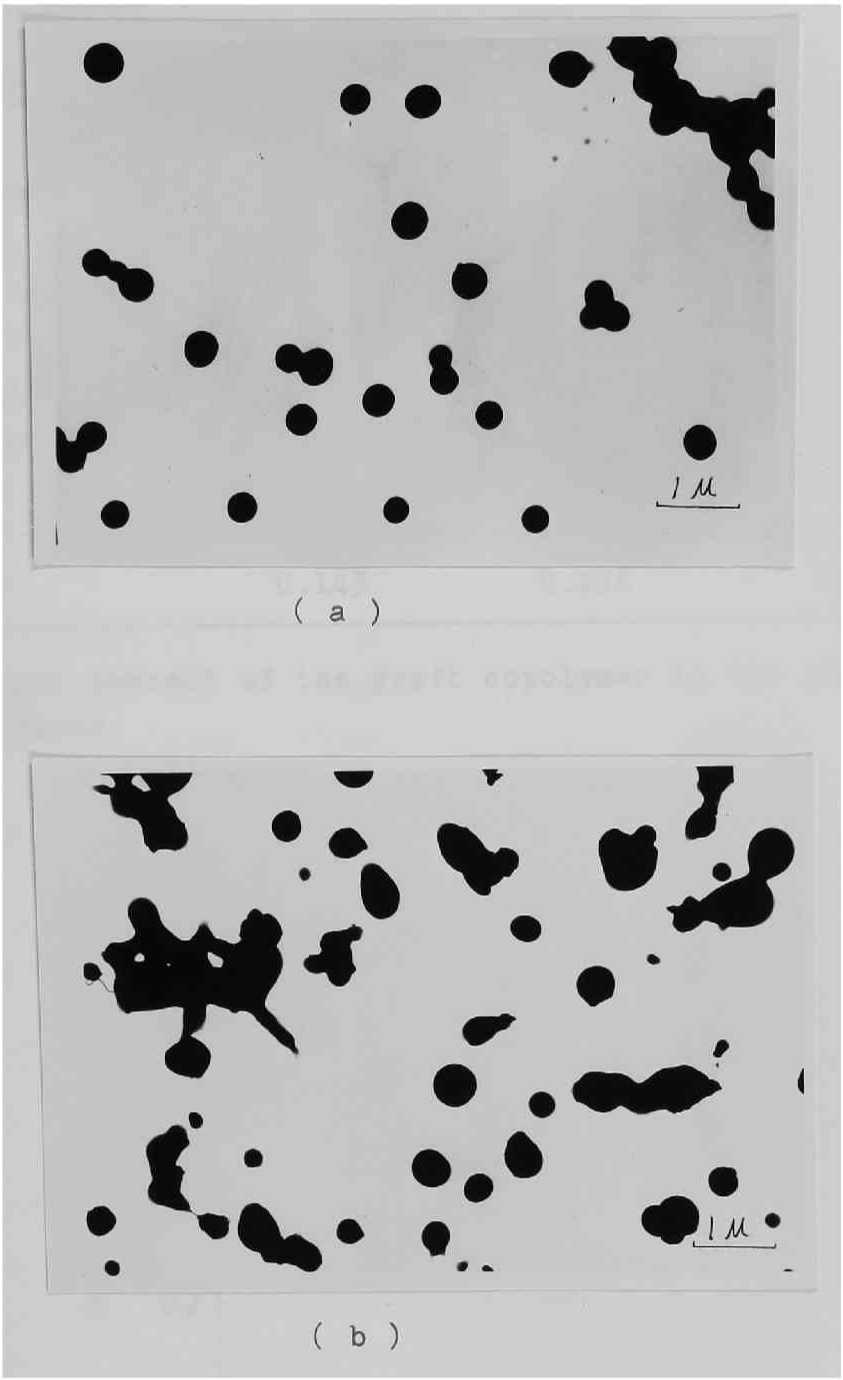


Fig. 7-8. Electron microscopic photographs of colloidal particles in the emulsion containing homoPMMA protected from precipitation by the presence of PVA-MMA graft copolymer. Concerning (a) and (b), see the text.

Table 7-1. Influence of the graft copolymer content on the radius of the emulsion particle.

GP content[a] (%)	$\bar{R}$ (μ)		
	DP of homopolymer		
	870	1,200	1,500
7.41	0.237	—	—
9.09	0.188	0.256	—
11.1	0.167	0.204	0.242
13.0	0.149	0.182	0.200
14.9	0.143	0.168	0.188

a) weight percent of the graft copolymer in the total polymers.

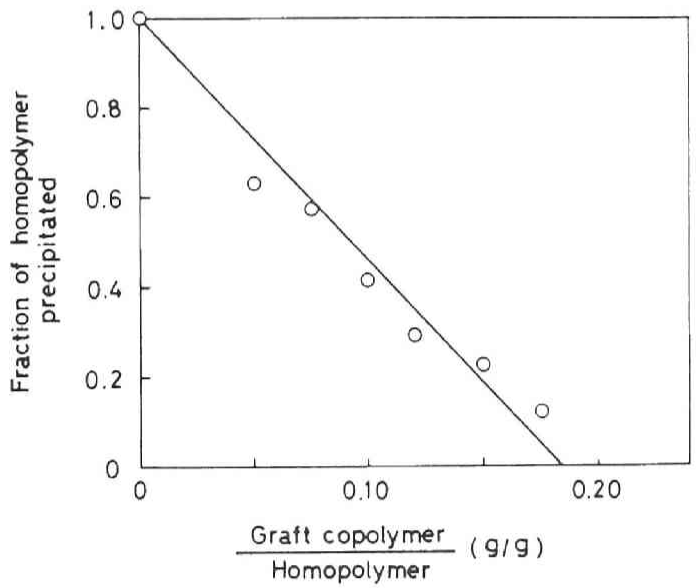


Fig. 7-9. Protection effect of PVAC-MMA graft copolymer on the precipitation of homoPMMA in DMSO-H_2O (DP = 1,500).

3. Polyvinyl acetate-MMA graft copolymer - homoPMMA system

The studies have been extended to poly(vinyl acetate)(PVAC)-MMA graft copolymer which was obtained by acetylation of the PVA portion of the PVA-MMA graft copolymer (M1M) used in the above experiment. The homopolymer to be emulsified is homoPMMA with DP of 1,500. The solvent-precipitant combination is DMSO-water, similarly to the case of PVA-MMA graft copolymer. The PVAC-MMA graft copolymer also was not precipitated by addition of such a small amount of water as to cause the homoPMMA to precipitate just to completion. Fig. 7-9 shows the results obtained. As can be seen clearly, this graft copolymer also protects homoPMMA significantly from precipitation.

DISCUSSION

As made clear in the above experiments, homoPMMA can be emulsified by both of the PVA-MMA and PVAC-MMA graft copolymers. According to a preliminary experiment, the PVA-MMA graft copolymer was found to be able to emulsify also homoPVA in DMSO-benzene mixture, where benzene is a good solvent for PMMA, but a precipitant for PVA. In this case, when the DMSO solution was poured into a large amount of benzene, the solution containing the emulsified PVA molecules seemed quite clear to the naked eye, but microscopically not homogeneous because Tyndall phenomenon was observed distinctly. Therefore, it may be concluded that the emulsification by a graft copolymer is not a specific effect observed only for some limited systems, but rather a general phenomenon and can be ascribed to the chemical structure characteristic to graft copolymers. (HomoPVA exhibited no protection effect for homoPMMA from precipitation.) The fact that colloidal dispersions of the homoPMMA are stable at least for six months, indicates the protecting force of graft copolymers to be relatively strong. It should be pointed out here that there is consequently considerable doubt as to whether the fractional and selective precipitation methods are really effective to separate the graft copolymer from the reaction mixture.

As is clearly seen from Figs. 7-5 and 7-6, such factors as

the graft copolymer and water contents affect greatly but complicatedly the emulsification of the homopolymer. First, we will discuss the emulsification mechanism in the region III of the phase diagram of Fig. 7-7, especially at the water content where all the homopolymer is just emulsified.

Region III : When the temperature of the solution containing both homopolymer and graft copolymer is decreased below the cloud point of the homopolymer, the homopolymer molecules should aggregate with each other, resulting in formation of such large particles that cause the appearance of solution turbid. It seems very reasonable to believe that the PMMA part in the graft copolymer is also incorporated into the particle formation, whereas the other soluble part cannot enter into the particle. Then it follows that the emulsion particles are surrounded by the PVA (or PVAC) part of the graft copolymer which is in a dissolved state regardless of the presence of the precipitant. As a result the particles may be held in dispersion by the soluble chains which form a peripheral outer shell, leading to prevention of coagulation of particles. This effect of graft copolymer seems analogous to the emulsification of organic liquids in aqueous solutions of soap. Electron microscopic photographs shown in Fig. 7-8 also support the above mechanism of emulsification. Then, the shell of a spherical emulsion particle should consist of monomolecular layer of graft copolymer, as illustrated schematically in Fig. 7-10. We can test the validity of this assumption by the following calculation.

The total surface area of particles in an emulsion of, say, 100 ml is given by

$$S = \sum_i n_i \cdot 4\pi R_i^2 \qquad (7\text{-}1)$$

where n_i is the number of particles with the radius of R_i in the 100 ml emulsion. The total number of graft copolymer molecules in the emulsion particles is

$$N_g = W_g \cdot \frac{N_A}{\bar{M}_g} \qquad (7\text{-}2)$$

where W_g is the weight of the graft copolymer present in the

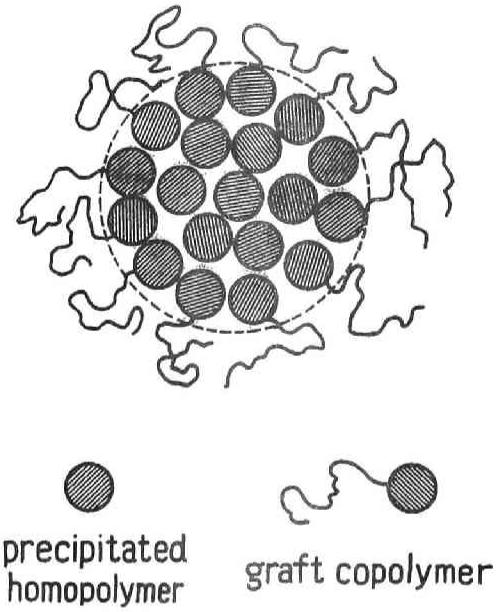


Fig. 7-10. Schematic representation of the protection mechanism.

100 ml emulsion, $\bar{M}_g$ is the number-average molecular weight of the graft copolymer and N_A is Avogadro's number. Since the total weight of particle in the 100 ml emulsion is $W_0 + W_g$, we obtain

$$W_0 + W_g = \sum_i n_i \cdot \frac{4}{3}\pi R_i^3 \cdot \rho \qquad (7\text{-}3)$$

where W_0 is the weight of homopolymer in the 100 ml emulsion and ρ is the density of the emulsion particles. Therefore, the particle radius is derived from the eqs.(7-1), (7-2), and (7-3) as a function of S_g which is defined as the average surface area distributed to one graft copolymer molecule and is equal to S/N_g.

$$\frac{\sum_i n_i \cdot R_i^2}{\sum_i n_i \cdot R_i^3} = \frac{1}{\bar{R}} = \frac{S_g}{3} \cdot \rho \cdot \frac{W_g}{W_0 + W_g} \cdot \frac{N_A}{\bar{M}_g} \qquad (7\text{-}4)$$

To verify this relation, the reciprocal of emulsion particle radius given in Table 7-1 was plotted against $W_g / (W_0 + W_g)$ in Fig. 7-11, where it can be seen that the experimental data satisfy the eq. (7-4) to a fairly good approximation. The S_g values calculated from the slopes of straight lines in Fig. 11 assuming $\rho = 1.188$ g/cm^3, are 6.3, 4.9 and 4.3 x 10^{-13} cm^2 for homoPMMA with DP of 870, 1200 and 1,500, respectively.

On the other hand, if each graft branch on the particle surface is assumed to have a spherical form, the cross sectional area of the sphere S' can be calculated from

$$S' = \pi \left(\frac{3}{4\pi} \cdot \frac{\bar{M}_b}{N_A} \right)^{2/3} \qquad (7\text{-}5)$$

where $\bar{M}_b$ is the number-average molecular weight of the branch PMMA. Again assuming $\rho = 1.188$, we find S' to be 4.4 x 10^{-13}

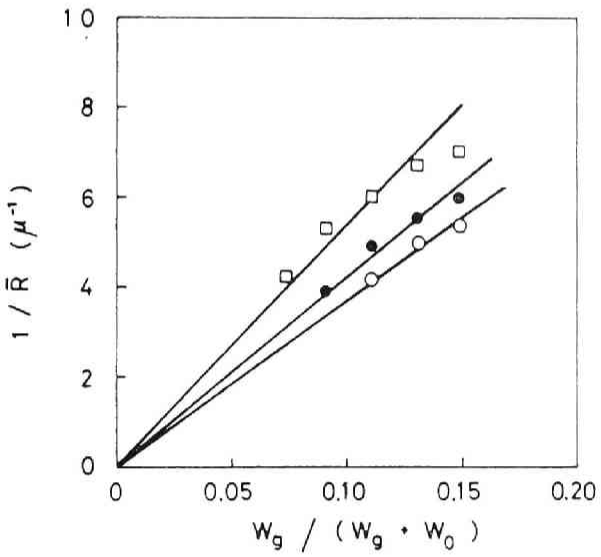


Fig. 7-11. $\frac{1}{\bar{R}} - \frac{W_g}{W_0 + W_g}$ plot according to the eq. (7-4).

○ : DP = 1,500, water content = 6.0 vol%

● : " = 1,200, " = 7.0 "

□ : " = 870, " = 7.5 "

cm^2. Agreement of this value with S_g is satisfactory, though S_g seems to increase slightly with decreasing DP of homoPMMA. This is a support for the mechanism of the emulsification that spherical emulsion particles have shells of monomolecular layer of graft copolymer.

Region I : Since the homopolymer is partly precipitated in this region, a small amount of the graft branch also must be coagulated. Nevertheless, the graft copolymer does not influence the phase separation of the homopolymer. It is at present difficult to give a clear explanation for this phenomenon. As is generally observed during the process to attain an equilibrium of liquid-liquid phase-separation, the solution becomes temporarily turbid upon addition of nonsolvent, and then separates gradually into two liquid layers. In the ini' l stage prior to the equilibri establishment, the graft copolymer with a precipitated branch might be located in the interface the unstable droplets present in the turbid solution as shown in Fig. 7-10, and hence to disturb the coalescence of each droplet which would lead otherwise finally to the phase-separation into two layers. If the density of the graft copolymer at the droplet surface is too sparse to prevent the droplet from the coalescence, no effect of the graft copolymer might be expected. This mechanism is somewhat similar to that of the polymeric oil-in-oil emulsion formation, as will be discussed in the following chapter. It might be better to state simply that the solution concentration of the graft copolymer should be higher than a critical value in order to emulsify the homopolymer, if one stresses the similarity of the present result with conventional emulsions where active surfactants are able to emulsify only when their concentration becomes higher than a so-called critical micelle concentration (CMC). If this is true, the graft copolymer content corresponding to the end of the plateau region in Fig. 7-5 should represent the CMC.

It is reasonable to suppose that the CMC decreases with increasing water content and finally becomes zero, because even one molecule of the graft copolymer is likely to protect a certain amount of the homopolymer.

Region II : As shown in Figs. 7-4 and 7-5, except for the homopolymer with the DP of 3,540, the fraction of the homopolymer precipitated decreases almost linearly with the graft copolymer content in the water content range where all the homopolymer is not yet precipitated (in the left side of the broken line in Fig. 7-7). This result suggests that a unit weight of the emulsifying graft copolymer protects constantly a definite amount of the precipitated homopolymer at a given water content.

When the water content becomes higher than that which precipitates just all the homopolymer (in the right side of the broken line in Fig. 7-7), the above-mentioned linearity is no longer observed (Fig. 7-6). In this case the emulsifying effect may become more remarkable, because the driving force to aggregate PMMA molecules should increase with increasing amount of the added precipitant. However, the strong aggregation of PMMA molecules might lead, in turn, to a result that an amount of the graft copolymer larger than what is sufficient just to emulsify the homopolymer is incorporated into the particles. Thus a somewhat excess amount of graft copolymer should be needed to emulsify all the homopolymer. This may be the main reason by which the boundary curve between the regions II and III goes upwards.

The other remarkable feature in the region II is that the emulsifying effect of the graft copolymer becomes much more significant with decreasing DP of the homopolymer, as is clearly seen in Fig. 7-4. This result may be explained in terms of aggregation velocity of PMMA chains. It is reasonable to suppose that the PMMA chains of higher DP must aggregate earlier than those of lower DP, because the precipitation equilibrium was established at 30°C by decreasing slowly the temperature of the solution from about 100°C where both of the homoPMMA and the graft copolymer were completely dissolved. Therefore, the homoPMMA molecule of DP higher than that of the graft branch PMMA (DP_0) is scarcely protected from precipitation by the graft copolymer, since the aggregated particle would have grown too large before the graft branches participate in the par-

ticle formation. However, in the present case every polymer sample has a rather broad DP distribution, and thus the emulsification of homoPMMA with higher $\overline{DP}$ than $\overline{DP}_0$ may occur to some extent. Of course, in this case the complete emulsification is impossible, as evidenced by the fact shown in Fig. 7-4 that it was not successful to emulsify all the homopolymer with the DP of 3,540. Furthermore, the extent of emulsification of the homopolymer was much lower, when the M7M graft copolymer (the average $\overline{DP}$ of branch = 1,500) was added. In the above consideration we ignored the effect of water content which was increased as the DP of homoPMMA became lower. However, this factor must be considered to discuss more deeply the effect of DP of homopolymer.

REFERENCES

1) L. J. Hughes and G. L. Brown, J. Appl. Polymer Sci., 7, 59 (1963).
2) G. E. Molau, J. Polymer Sci., A, 3, 1267, 4235 (1965).
3) J. D. Wellons, J. L. Williams and V. Stannett, J. Polymer Sci., A-1, 5, 1341 (1967).
4) G. Riess, J. Kohler, C. Tournut and A. Banderet, Makromol. Chem., 101, 58 (1967).
5) A. Banderet, C. Tournut and G. Riess, J. Polymer Sci., C, 16, 2601 (1967).
6) J. Kohler, G. Riess and A. Banderet, European Polymer J., 4, 173 (1967).
7) G. E. Molau, Characterization of Macromolecular Structure, edited by N. R. C., Nat. Acad. Sci., Washinton, D. C. 1968, p. 245. The References are collected in this review.
8) T. Inoue, T. Soen, T. Hashimoto and H. kawai, Macromolecules, 3, 87 (1970).
9) A. Skoulios, P. Helffer, Y. Gallot and J. Selb, Makromol. Chem., 148, 305 (1971).

CHAPTER 8

EFFECT OF GRAFT COPOLYMER ON DEMIXING OF IMMISCIBLE POLYMERS IN SOLUTION

INTRODUCTION

In the preceding chapter we have shown that graft copolymers are able to emulsify a large amount of constituent homopolymer in selective solvents in which the graft copolymers are in a "dissolved" state, whereas the homopolymer is in a "precipitated" state. This emulsifying ability of a graft copolymer seems to be related to its characteristic chemical structure. Indeed, the graft copolymer as well as the block copolymer may be regarded as an amphiphilic compound (1), such as surfactants of low molecular weight, since these copolymers comprise polymer sequences of chemically different segments in the same molecule.

It seems likely that even in a good solvent for both the backbone and the grafted branch the interaction between chemically different segments may cause a segregation of each polymer sequence in the graft copolymer molecule, at least in relatively concentrated solutions (2). Hence the graft copolymer molecules may be segregated into micelles above a certain threshold concentration, though there is still controversy concerning the molecular conformation in very dilute solutions (3). Vanzo(4) concluded the micelle to be formed from the fact that solutions of a block copolymer showed iridescent colors at moderate concentrations.

On the other hand, as is well known, a solution of immiscible homopolymers in a common good solvent separates into two phases and demixes gradually on standing due to incompatibility of the polymers. If the demixing into layers could be prevented by some means, a stable (in reality, metastable) emulsion would be obtained. Molau (5) first pointed out that such an emulsion should be actually formed when a graft or block copolymer is present in immiscible polymer solutions, because the copolymer can act as an emulsifier. An emulsion of this class is termed as polymeric oil-in-oil emulsion (POO emulsion).

Recently Okada and his collaborators (6) reported that the demixing rate of dimethylformamide solutions of a polyacrylonitrile-poly(vinyl chloride) blend is greatly reduced by addition of a small amount of the grafting product obtained by polymerization of acrylonitrile in poly(vinly chloride) powder.

Thus it seems highly probable that an emulsifying effect of the graft copolymer would be observed also in a good solvent. The aim of the present work was to study the effect of a graft copolymer on the demixing of immiscible polymer solutions and to find the critical conditions for the formation of stable POO emulsion, especially as a function of the graft copolymer and blend polymer concentrations and the degree of polymerization of homopolymers. Molau (7) has recently investigated the influence of molecular weight of a block copolymer on the stability of a POO emulsion.

EXPERIMENTAL

1) Graft copolymer

Graft copolymer consisting of one PVAC backbone and one PS branch was obtained by complete acetylation of the PVA part of a PVA-styrene graft copolymer (M4S) prepared by radiation graft copolymerization of styrene onto PVA as shown in Chapter 3. The number-average degrees of polymerization (DP) of the branch and the backbone were 1,880 and 2,350, respectively. The detailed grafting procedure and the characterization method were described in Chapter 3.

2) Homopolymers

Samples of homoPVAC were prepared by acetylation of commercial PVA with a viscosity-average DP of 420, 430 and 1,000. HomoPS samples were obtained by thermal polymerization of styrene in the presence of carbon tetrachloride. The viscosity-average DP was 510, 590, 950 and 1,030.

3) Preparation of emulsions and measurement of the stability

PVAC and PS were weighed into a test tube to which 1 - 0.1 % benzene solution of PVAC-styrene graft copolymer and pure benzene were added to obtain a desired concentration of the polymers. After the test tube was sealed and the polymers were completely dissolved, the solution mixture was shaken vigorously with the use of a vibromixer.

In the case to compare the instability of emulsions at low homopolymer concentrations, the time necessary for the incipient demixing at room temperature was measured. On the other hand, for emulsions of higher concentrations, the point at which the demixing begins could not be determined visually with reasonable accuracy owing to the high turbidity. Therefore, in this case we pursued the turbidity change of the emulsion with time by means of a turbidimeter. Fig. 8-1 represents one of typical changes of the relative turbidity of emulsions at various blend concentrations under a constant wt. ratio of graft copolymer (GP) to PVAC. The blend concentration is always expressed in the present work, unless otherwise mentioned, as $[(W_{PS} + W_{PVAC})/(W_{PS} + W_{PVAC} + W_{benzene})] \times 100$, where W is the weight of sub-

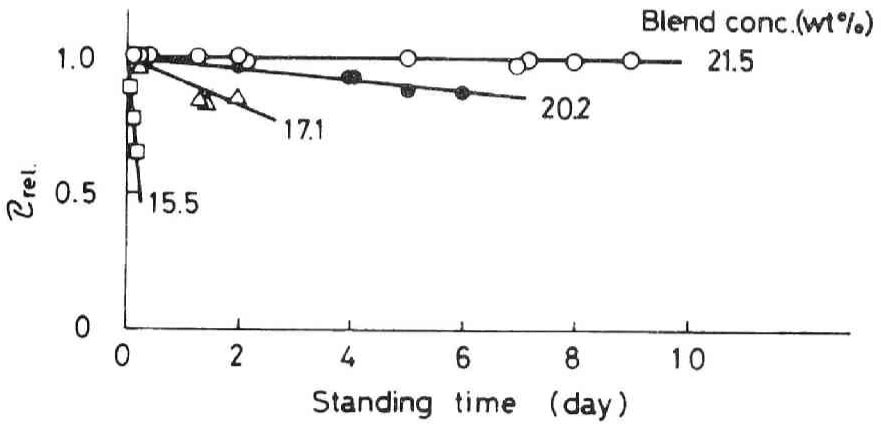


Fig. 8-1. Change of the relative turbidity $\tau_{rel.}$ with standing time (PVAC/PS = 1/4, GP/PVAC = 0.10).

stance denoted by the subscript. The turbidity seems to change approximately linearly with the time of standing, at least, in the initial stage. Thus a plot of the initial slope of curves against the blend concentration (Fig. 8-2) enables us to determine the critical point of stable emulsion formation.

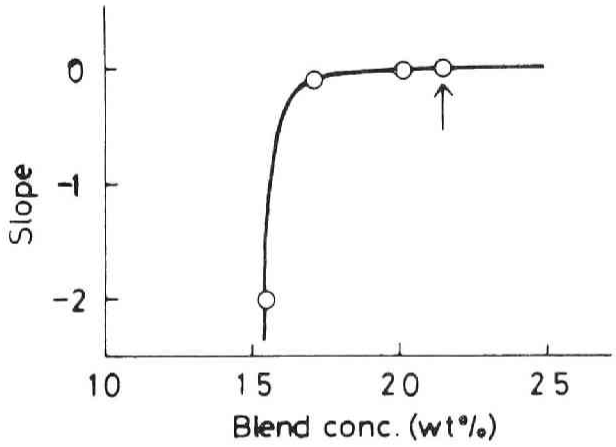


Fig. 8-2. Influence of the blend concentration on the rate of turbidity change (PVAC/PS = 1/4, GP/PVAC = 0.10).

The critical blend concentration required to form a stable emulsion is indicated in Fig. 8-2 by an arrow, where the slope becomes just zero.

4) Phase-contrast microscopy and electron microscopy

A phase-contrast microscope was used for emulsions and an electron microscope for dried sample. The latter was made by casting the emulsion on a glass plate and evaporating benzene, and then cutting into ultrathin sections of about 800 Å thickness. In order to contrast the PS region with PVAC, PVAC was extracted selectively from the ultrathin section with methanol. Consequently samples from a 1 : 4 blend of PVAC and PS could be observed with the electron microscope, because only in this case the PVAC phase was dispersed in the form of droplets in the continuous PS phase.

RESULTS

1) Formation of POO-emulsion

Fig. 8-3 shows the influence of graft copolymer on the demixing of blend solutions.

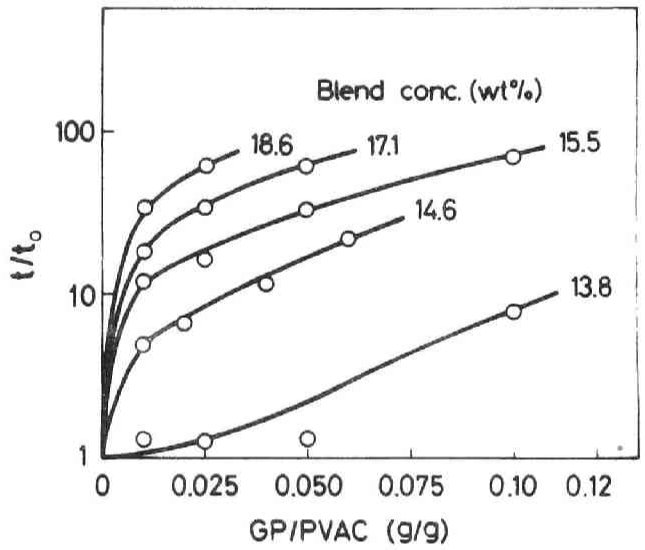


Fig. 8-3. Effects of the graft copolymer content and the blend concentration on the time for incipient demixing (PVAC/PS = 1/4).

The wt. ratio of PVAC to PS was kept at 1/4 and the DP's of PVAC and PS were 430 and 590, respectively. The blend concentrations studied here are rather close to the critical blend concentration for demixing, which is 13 wt% in the present case. The graft copolymer content was expressed by wt. ratio of the graft copolymer to the homopolymer corresponding to the dispersed phase component. The value of t/t_0 in ordinate is the ratio of the time required for the incipient demixing in the presence of the graft copolymer to that in the absence of it. It is clear from Fig. 8-3 that t/t_0 becomes as high as about 100 in this blend concentration range, but tends to level off with increasing graft copolymer content. This implies that stable emulsions would not

be formed even if a rather large amount of the graft copolymer is added, so long as the blend concentration remains low.

Therefore we made a further experiment at higher blend concentrations and followed the turbidity change. In this case stable emulsions were found to be successfully formed. As can be seen from Fig. 8-4, where the minimum graft copolymer contents required for emulsion formation were plotted against the blend concentration, they decrease progressively with the blend concentration and are so small as about 1/10 of the amount of PVAC or 1/50 of the total polymer blend at a blend concentration of 21.5 wt%.

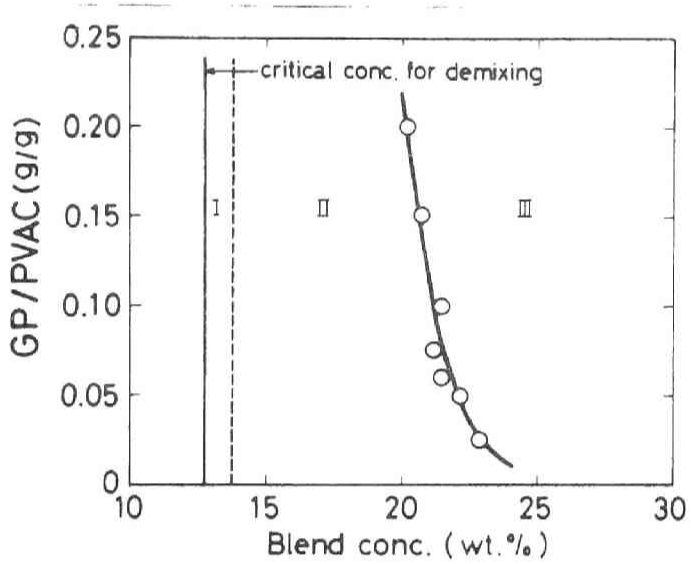


Fig. 8-4. Phase diagram of POO emulsion (PVAC/PS = 1/4).

The stable emulsions formed in the region III were very turbid and the appearance did not change within a few months. On the contrary, in the region II, where the blend concentrations correspond to those studied in Fig. 8-3, stable emulsions were not formed, but merely the reduction in demixing rate was observed on addition of the graft copolymer. When the blend concentration was very close to the critical blend concentration for demixing (region I), the graft copolymer did not practically influence

the demixing behavior.

The effect of the blend ratio of two homopolymers on formation of stable emulsions is shown in Fig. 8-5.

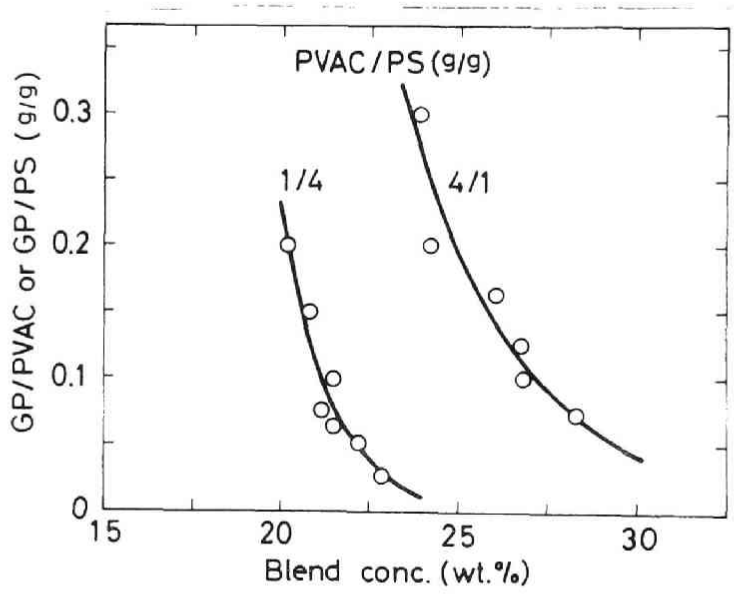


Fig. 8-5. Influence of the blend ratio (PVAC/PS) on the emulsification.

The critical demixing concentration for the blend of PVAC/PS = 4/1 was nearly identical to that of PVAC/PS = 1/4. Nevertheless, the lowest blend concentrations for the stable emulsion formation are quite different between the two blends.

2) Microscopy of POO emulsions

The POO emulsions were examined by a phase-contrast microscope. Fig. 8-6 shows a representative microscopic photograph taken under the following conditions ; PVAC/PS = 1/4, GP/PVAC = 0.10 and the blend concentration = 21.5 wt%. The white part of the photograph corresponds to PVAC solution droplets and the gray continuous part to PS solution phase. For the blend with PVAC/PS = 4/1, the phase was inverted as shown in Fig. 8-7.

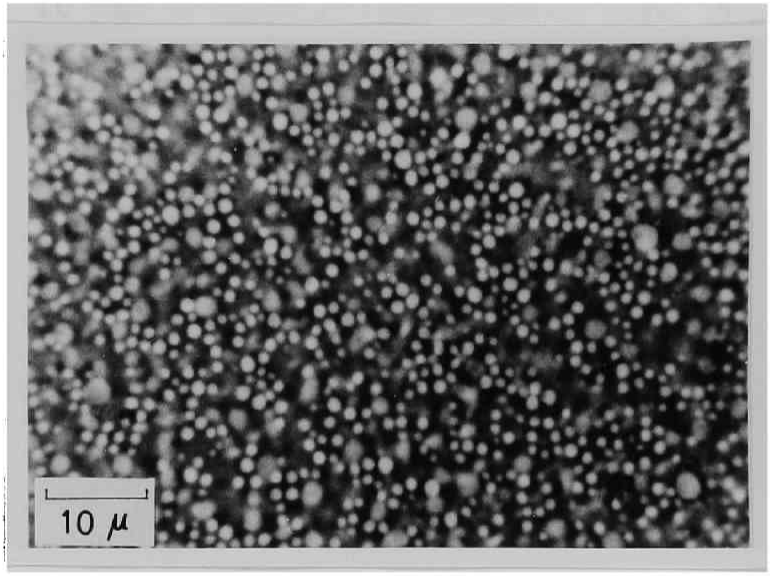


Fig. 8-6. Phase-contrast microscopic photograph of an emulsion (PVAC/PS = 1/4, GP/PVAC = 0.10, Blend conc. = 21.5 wt%).

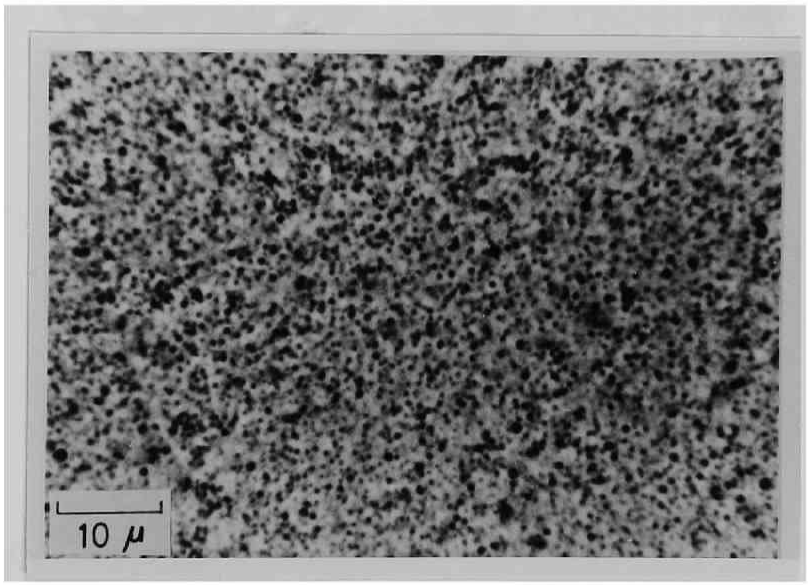


Fig. 8-7. Phase-contrast microscopic photograph of an emulsion (PVAC/PS = 4/1, GP/PS = 0.15, Blend conc. = 27.4 wt%).

In both the photographs it is seen that the droplet size distribution is fairly uniform, similarly as observed by Molau(5). The difference in the droplet radius between Figs. 8-6 and 8-7 is remarkable. The droplets formed in an unstable region were observed to change rapidly to larger and less uniform ones by successive coagulation of droplets.

It seems interesting to see whether the emulsion structure is preserved even after the solvent is vaporized. For this purpose the same emulsion as shown in Fig. 8-6 was dried and an ultrathin section was prepared to observe by an electron microscope. The photograph is given in Fig. 8-8 . Since PVAC was extracted from the sample with methanol to distinguish the PVAC region from that of PS, the dispersed phase appears white in the photograph. It is clearly seen that the emulsion structure is retained still in the dried state.

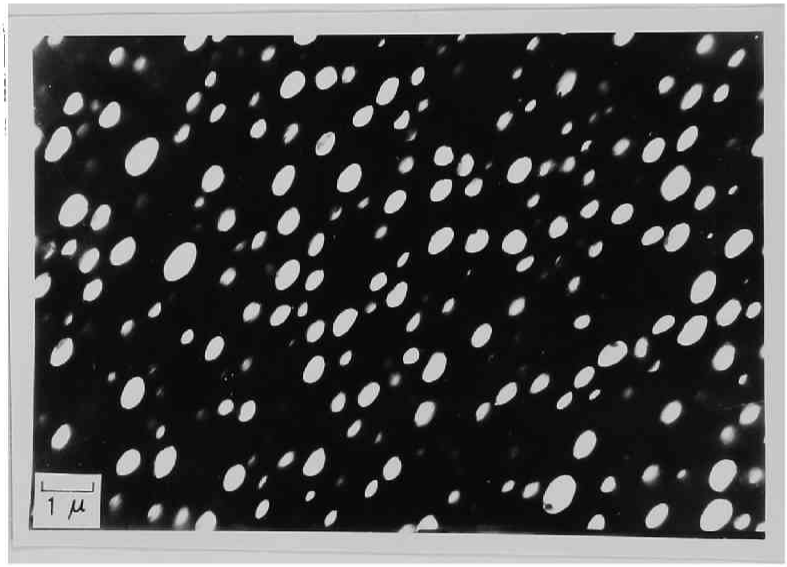


Fig. 8-8. Electron micrograph of an ultrathin section of the film prepared by drying an emulsion (PVAC/PS = 1/4, GP/PVAC = 0.10, Blend conc. = 21.5 wt%).

As can be supposed from Figs. 8-3 and 8-4, such finely dispersed structure may not be generated by means of simple casting from dilute homogeneous solutions, since droplets of the polymer solution will coagulate with each other already in an unstable region (region II in Fig. 8-4) during evaporation of the solvent.

3) Factors governing the droplet radius

In order to obtain some deeper insight into the mechanism of stabilization of the POO emulsion, the change in size of emulsion droplets was investigated as a function of various factors. The size was read from the phase-contrast microscopic photographs. The influence of graft copolymer content on the droplet radius is given in Fig. 8-9, where the results obtained in the unstable region II (GP/PVAC < 0.075) are also plotted for comparison.

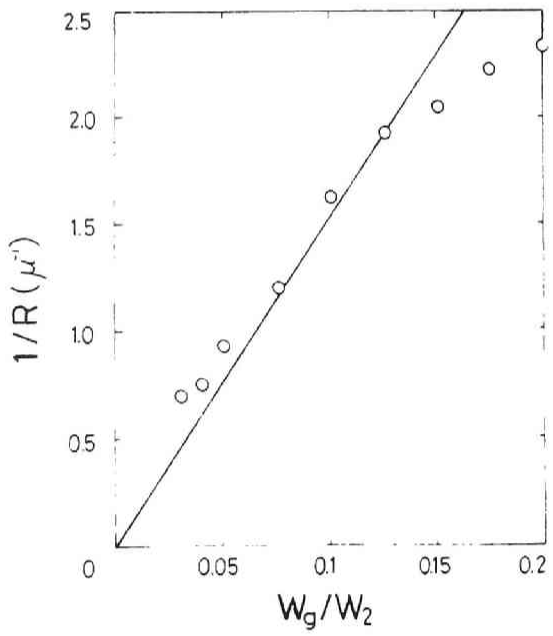


Fig. 8-9. The plot of reciprocals of droplet radius R against the graft copolymer content W_g/W_2 (PVAC/PS = 1/4, Blend conc. = 21.5 wt%).

It is seen that the droplet radius varies inversely with the graft copolymer content in the stable region, though some deviation takes place at higher graft copolymer contents.

Fig. 8-10 shows the influence of the DP of each homopolymer on the droplet radius. Evidently the droplet radius does not depend on the DP of each homopolymer within the DP range studied. The droplet size distribution was very uniform, as mentioned above. It was observed, however, that the droplets became very large and no longer had a narrow size distribution when the DP of homopolymers exceeded about 1,000. This suggests that such emulsions are unstable. A similar result was reported also by Molau (7), who pointed out that the broader size distribution in the higher molecular weight range depends simply on a dispersion method. The dependence of the droplet size on the blend concentration is shown in Fig. 8-11.

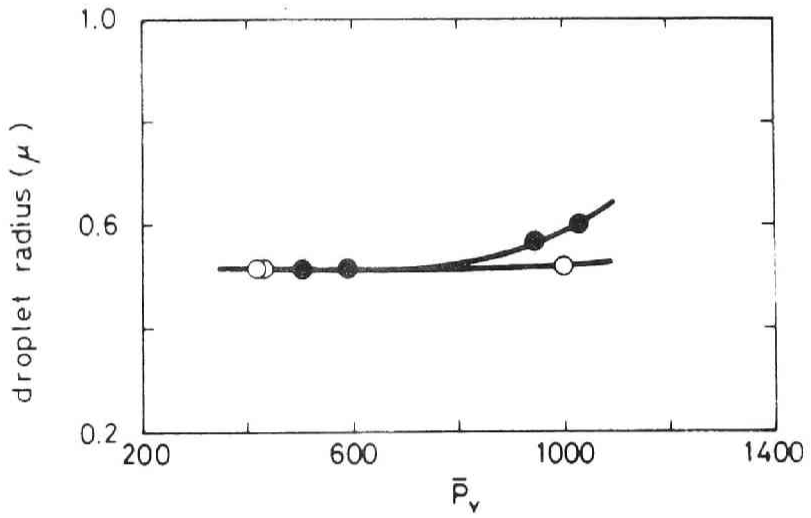


Fig. 8-10. Influence of the degree of polymerization of the homopolymers on the droplet radius (PVAC/PS = 1/4, GP/PVAC = 0.125).
○ : homoPVAC (DP of homoPS = 590)
● : homoPS (DP of homoPVAC = 430)

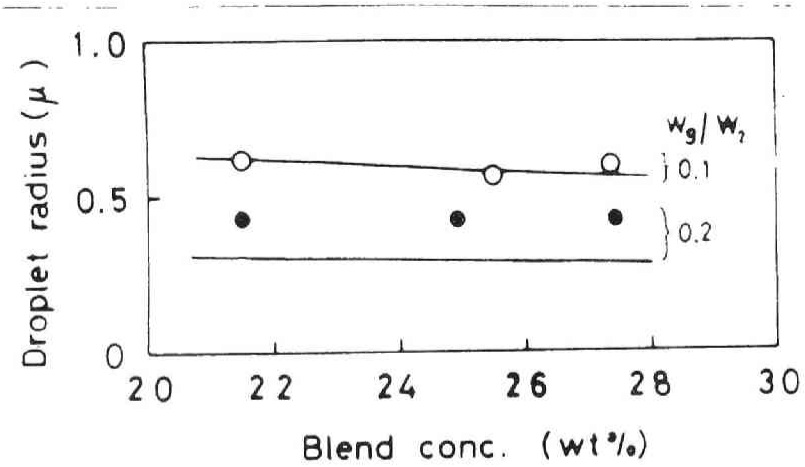


Fig. 8-11. Influence of the blend concentration on the droplet radius (PVAC/PS = 1/4).
○ , ● : experimental results
—— : according to the eq.(8-5)

It is seen that the variation of radius with the blend concentration is insignificant. The curves in Fig. 8-11 will be discussed later.

DISCUSSION

It is evident from the results obtained above that the PVAC-styrene graft copolymer has a large effect on the demixing of PVAC-PS-benzene mixture. For instance, stable emulsions are formed upon addition of the graft copolymer by an amount of only about 1/10 of the dispersed component polymer or about 1/50 of the total polymer blend, unless the blend concentration is lower than a certain critical value.

Before we discuss the mechanism of stabilization of emulsion, we should first consider the efficiency of the emulsifying method with a vibromixer. It might be reasonable to suppose that dispersion of droplets takes place only to an insufficient extent, if the blend mixture has high viscosity such as at high polymer concentrations or high DP. In fact, it was observed that the emulsion droplet size became abnormally large and quite nonuniform for the homopolymers with DP higher than about 1,000. However, in the emulsions made from the homopolymers with DP smaller than

1,000, the distribution of droplet size was quite narrow, and the reproducibility of the data was quite satisfactory. Thus the emulsifying method with a vibromixer may be regarded as an efficient procedure in the present study, where the homopolymers with DP smaller than 1,000 were used.

Molau(5) proposed the following mechanism for the stabilization of POO emulsion. The graft copolymer molecules accumulate in the interface between the droplet and the continuous phase owing to the repulsive interaction between chemically different polymer chains. As the droplets covered with graft copolymers are brought closer together to interpenetrate with each other, significant repulsion should arise from the increase in the local concentration of the polymer chains at the overlapping interface and, in addition, from the incompatibility of different polymer chains, leading to protection of droplets against coalescence. The former is just the same repulsive force as interacting between particles adsorbed by dissolved polymeric chains in a lyophilic dispersion. Stabilization of the dispersion has been considered to be due to the repulsive forces resulting from the possible change in the free energy of mixing of polymer and solvent(8-11) occurring when chain molecules adsorbed on neighboring particles begin to overlap. We also intended to discuss in some detail the mechanism of the flocculation of graft copolymer micelle in a selective solvent and the origin of the repulsive force. It will be given in the next chapter.

It should be noted that in POO emulsion both components of the emulsifying graft copolymer have a nearly similar solubility to the solvent and that amphiphilic behavior may result from the incompatibility of chemically different polymers. This feature, characteristic of POO emulsions, can account for the fact that the emulsifying effect of graft copolymer in a good solvent is greatly affected by the blend concentration (Fig. 8-4). Of course, the graft copolymer molecule is thought to undergo intramolecular phase separation and to accumulate preferably in the interface, even in regions I and II. However

it seems plausible that the graft copolymer molecules are not fixed strongly enough in the interface to prevent the coalescence of droplets, but rather mobile because of insufficient attractive interaction between the homopolymer and the similar component of the graft copolymer. On the contrary, as the blend concentration becomes higher, the interaction between similar segments will be enhanced probably due to decrease in solvation caused by different segments and increase in viscosity. As a result, the graft copolymer molecules would be fixed sufficiently in the interface to prevent the coalescence of droplets.

It may be interesting to point out here that the fixation of the graft copolymers in the interface between solution droplets and the intervening continuous solution phase becomes more strong and stable if the disperse phase is not in a mobile fluid state but in a solid state such as crystalline or glassy. When the precipitant of the polymer in the dispersed phase is added to the solution, the mobile, dissolved polymer chains change to precipitated ones. Consequently, the mobility of the polymer molecules must be remarkably reduced and a strong aggregative force may arise to give good emulsion stability. This is just the case studied in the preceding chapter.

On the basis of the simplified mechanism that every graft copolymer molecule is located in the interface between the droplet and the continuous phase in the emulsion, it is possible to derive equations relating the droplet radius R to the blend concentration and the graft copolymer content, provided that each graft copolymer molecule occupies a definite interface area S_g and the whole interface area of the stable emulsion droplets is entirely covered with the monolayer of graft copolymers. If an emulsion of 100 ml contains N_e droplets and N_g graft copolymer molecules, we obtain

$$N_g \cdot S_g = \frac{W_g}{M_g} \cdot N_A \cdot S_g = 4\pi R^2 \cdot N_e \qquad (8\text{-}1)$$

where W_g is the weight of the graft copolymer in 100 ml emulsion,

$\bar{M}_g$ is the number-average molecular weight of graft copolymer, and N_A is Avogadro's number. The total dispersed phase volume V_2 in 100 ml emulsion is given by

$$V_2 = (4\pi R^3 / 3) \cdot N_e \qquad (8\text{-}2)$$

As is seen from Table 8-1, the blend solutions containing no graft copolymer demix into two phases whose volume fraction is nearly equal to the weight fraction of each added homopolymer at higher concentrations. A similar result was also obtained by Sakurada about 25 years ago (12). Therefore V_2 can be taken to be approximately equal to 100 x $W_2/(W_1 + W_2)$ in the stable emulsion region, where W_1 and W_2 are the weight of the homopolymer corresponding to the continuous and dispersed component in the 100 ml emulsion, respectively. Substituting these relations into eq. (8-1), we get finally the following relation.

$$R \cdot \frac{W_g}{W_2} = \frac{300 \cdot \bar{M}_g}{(W_1 + W_2) \cdot S_g \cdot N_A} \qquad (8\text{-}3)$$

The graft copolymer content defined in the present study is W_g/W_2. According to eq. (8-3), R should be inversely proportional to W_g/W_2 , when $W_1 + W_2$ is kept constant and S_g is assumed not to depend on the concentration of graft copolymer. This assumption may be correct to a first approximation, since the graft copolymer content is quite low in the present case. The experimental results in Fig. 8-9 seem to obey eq. (8-3). The deviation seen at graft copolymer contents lower than 0.075 might be ascribed to the fact that the emulsions are in the unstable state where eq. (8-3) is no longer valid. The deviation at relatively high graft copolymer contents may be due to rather insufficient mixing to generate equilibriated emulsion.

Applying eq. (8-3) to the experimental results, we can confirm the assumption that the droplets are covered by monolayers of graft copolymer molecules. As is seen from Fig. 8-9, when W_g/W_2 is, for example, 0.1, R is 0.62μ. As the blend concentration is 21.5 wt%, that is, (21.5 g blend) / (100 g blend solution), $W_1 + W_2$ amounts to approximately 19.7 g in 100 ml

Table 8-1. Influences of the DP of each homopolymer, the total blend concentration and the blend composition on the volume fraction of two separated phases.

DP		blend concentration		wt. fraction of PVAC in blend	volume fraction of PVAC rich phase
PVAC	PS	(wt%)	(vol%)[a]		
430	590	14.7	13.3	0.20	0.15
"	"	18.7	17.1	"	0.19
"	"	22.4	20.6	"	0.20
"	"	25.7	23.7	"	0.21
"	"	28.8	26.8	"	0.21
"	950	22.4	20.6	"	0.20
"	1,030	"	"	"	0.20
420	590	"	"	"	0.20
1,000	"	"	"	"	0.20
430	"	"	"	0.80	0.84
"	"	25.7	23.7	"	0.80
"	"	28.8	26.8	"	0.81

a) Calculated under the assumption of no volume change at dissolution.

emulsion, provided that the simple additivity of solute polymers and the solvent holds for the emulsion volume and that the density of both polymers in emulsion is 1.1. Substituting these values and $\bar{M}_g = 3.90 \times 10^5$ into the eq. (8-3), we find S_g to be 1.57×10^{-12} cm^2.

On the other hand, the volume shared per gram polymer in the emulsion is simply $100/(W_1 + W_2)$, since 100 ml emulsion contains the blend polymers of $(W_1 + W_2)$ gram. Also the branch PS and the backbone PVAC may be assumed to occupy the similar volume in the emulsion. Then the volume to be distributed, for instance, per branch PS molecule is

$$\frac{100}{W_1 + W_2} \cdot \frac{\bar{M}_b}{N_A},$$ where $\bar{M}_b$ is the molecular weight of the branch.

Therefore, if we reduce the volume to a sphere, the cross-sectional area of the sphere S' is given by

$$S' = \pi \left(\frac{3}{4\pi} \cdot \frac{\bar{M}_b}{N_A} \cdot \frac{100}{W_1 + W_2} \right)^{2/3} \qquad (8\text{-}4)$$

The similar equation can be obtained also for the backbone PVAC. The calculated S' values are 1.62×10^{-12} cm^2 for branch PS and 1.75×10^{-12} cm^2 for backbone PVAC molecule. These values agree fairly well with the interfacial area S_g shared per graft copolymer which is calculated under the monolayer assumption. We believe that this finding affords strong support for the above mechanism; every graft copolymer molecule accumulates in the interface, covering compactly the droplet surface.

Therefore, if we assume S_g to be equal to S' and substitute the eq. (8-4) into the eq. (8-3), we get the following equation.

$$R = \left(\frac{4.8 \times 10^3}{\pi N_A} \right)^{1/3} \cdot \frac{\bar{M}_g}{\bar{M}_b^{2/3}} \cdot \frac{W_2}{W_g} \cdot \frac{1}{(W_1 + W_2)^{1/3}} \qquad (8\text{-}5)$$

The curves given in Fig. 8-11 were plotted according to the eq. (8-5), converting $W_1 + W_2$ into the blend concentration expressed

in wt%. As can be seen from Fig. 8-11, the curve agrees quite well with the experimental results obtained at $W_g/W_2 = 0.1$. The disagreement at $W_g/W_2 = 0.2$ is ascribed to the fact that the radius of emulsion droplets does not vary anymore inversely proportional to W_g/W_2 at such high graft copolymer content range. The prediction of the eq. (8-5) that R is independent of DP of the homopolymers was confirmed by the results shown in Fig. 8-10.

In conclusion, it may be summarized that each graft copolymer accumulates on the surface of the droplets and occupies a definite area. As the blend concentration exceeds a threshold value, the graft copolymer is fixed strongly enough on the droplet surface to hinder the coagulation of droplets, leading to formation of stable emulsions. There are two factors influencing the droplet size in the stable region; the graft copolymer content and the interface area occupied by each graft copolymer molecule.

REFERENCES

1) For example, P. A. Winsor, Chem. Rev., 68, 1 (1968).
2) For example, H. Benoit, Ber. Bunsenges. Physik. Chem., 70, 286 (1966) ; G. E. Molau, "Characterization of Macromolecular Structure", Chapter 3, ed. D. McIntire (Nat. Acad. Sci., Washington, D. C., 1968).
3) For example, A. Dondos, P. Rempp and H. Benoit, Makromol. Chem., 130, 233 (1969) ; H. Ohnuma, T. Kotaka and H. Inagaki, Polymer J., 1, 716 (1970).
4) E. D. Vanzo, J. Polymer Sci., A-1, 4, 1727 (1966).
5) G. E. Molau, J. Polymer Sci., A, 3, 1267, 4235 (1965).
6) T. Okada, K. Yamazaki and I. Sakurada, JAERI, 5027, 35 (1971).
7) G. E. Molau, Kolloid-Z. u. Z. Polymere, 238, 493 (1970).
8) D. J. Meier, J. Phys. Chem., 71, 1861 (1967).
9) E. W. Fischer, Kolloid-Z., 160, 120 (1958).
10) D. H. Napper, Trans. Faraday Soc., 64, 1701 (1968).
11) R. H. Ottewill and T. Walker, Kolloid-Z. u. Z. Polymere, 227, 108 (1968).
12) I. Sakurada, Gendai Koshitsugaku Tenbo, 1, 77 (1948).

CHAPTER 9

THE FORMATION AND FLOCCULATION OF GRAFT COPOLYMER MICELLES

INTRODUCTION

It is well known that graft and block copolymers are able to form micelles by themselves in a common good solvent at high concentrations as well as in a selective solvent(1,2). In addition, it has recently been made clear that they can emulsify the corresponding homopolymers(3 - 14) and low-molecular-weight compounds (15 - 17). These phenomena result obviously from the fact that they are a kind of amphiphilic compounds(18) which are characterized by possessing in the same molecule two groups or sequences greatly different in their solubility behavior.

Up to the present time, extensive works have been reported for the dilute solution properties of the copolymers(1,2). However, less attention has been given towards the aggregation process of the graft and block copolymers as nonionic polymeric amphiphiles.

In this chapter criteria for formation and flocculation of the graft copolymer micelles were investigated turbidimetrically in single selective solvents and the formed micelles were observed by electron microscopy. We used as graft copolymers PVAC-styrene graft copolymers with one branch whose length is comparable to that of the backbone and PVAC-MMA graft copolymers with one or several branches.

EXPERIMENTAL

1) Graft copolymers

PVAC-styrene and PVAC-MMA graft copolymers with one branch were synthesized by complete acetylation of PVA part of PVA-styrene and PVA-MMA graft copolymers prepared by mutual irradiation graftings of styrene and MMA onto PVA films, respectively. PVA-MMA graft copolymers with several branches were prepared by chemical grafting of MMA onto PVA in homogeneous dimethyl sulfoxide solution with the use of potassium persulfate as an initiator as shown in Chapter 5 and then converted to PVAC-MMA graft copolymers.

Table 9-1. Characteristics of PVAC-styrene and PVAC-MMA graft copolymer samples.

Sample[a)]	VAC content (wt%)	$\bar{M}_n \times 10^{-5}$			Number of branches
		Graft copolymer	Backbone	Branch	
M3S	63.1	3.54	2.23	1.04	1.26
M8S	48.2	2.89	1.39	1.41	1.06
M9S	58.9	4.02	2.36	1.40	1.18
M10S	48.4	6.03	2.92	2.71	1.15
M3M	37.0	3.02	1.12	1.87	1.02
M7M	60.5	3.95	2.39	1.56	1.00
DG-2	28.3	10.9	3.09	1.99	3.92
DG-4	34.6	6.12	2.12	1.52	2.63
DG-5	28.2	8.51	2.40	1.95	3.13

a) MXS : The backbone is PVAC and the branch is PS.
MYM, DG-Z : The backbone is PVAC and the branch is PMMA.

These graft copolymers were freed from the corresponding homopolymers by vigorous alternate extraction and their purity was checked by thin-layer chromatography. The chemical structure of the graft copolymers used in the present study is summarized in Table 9-1.

2) Homopolymers

PVAC homopolymers were obtained by acetylation of commercial PVA's with an acetic anhydride-pyridine mixture(1 : 2). PS and PMMA homopolymers were those which were formed during the above grafting reactions. As a monodisperse sample NBS 705 standard

PS was used. Their number-average molecular weights are summarized in Table 9-2.

Table 9-2. $\bar{M}_n$ of PVAC, PS and PMMA homopolymer samples.

	PVAC-1	PVAC-2	PS-1	PS-2	PS-3	PS-4[a)]	PMMA-1
$\bar{M}_n \times 10^{-5}$	0.664	1.15	1.22	2.11	6.50	1.709	4.15

a) NBS 705.

3) Turbidimetry

The turbidity which appeared upon cooling a polymer solution under stirring was measured by a Shimazu-Kotaki photoelectric nephelotitrator NT.3H with the incident light of 436 nm from a mercury lamp and recorded as optical density. About 180 ml of the solution in a cylindrical cell was cooled or heated at a rate slower than 0.5°C per minute by circulating poly(ethylene glycol) from a thermostat. The temperature of the solution was measured directly, putting a thermometer in the cell. As the turbidity difference was slight between the precipitated and dissolved state of the graft copolymers, all incipient cloud points were determined by the scattered light at 90°. The total polymer concentration was adjusted to 5 - 200 mg in 100 ml solution.

4) Determination of θ-temperature

The θ-temperatures(T_θ) were determined osmometrically from dependence of the second virial coefficient on the temperature. A 502-type high-speed membrane osmometer (Hewlett Packard Co.) was used.

5) Electron microscopy

Electron micrographs were taken after the solution contain-

ing micelles was dialyzed against methanol or acetonitrile and condensed to dryness on carbon-reinforced poly(vinyl formal) film at room temperature followed by platinum-shadowing. The dialysis was performed because of low vapor pressure of the solvent used for the micelle formation. For comparison the micrographs were also taken without dialysis.

RESULTS AND DISCUSSION

1) Formation of graft copolymer micelles

As shown in Chapter 6, the dried samples of graft copolymers are often observed to be spontaneously dispersed into selective solvents to form micelles. The dispersibility depends strongly on the affinity of the solvent to the insoluble chain as well as the solvent-precipitant combination with which the dried sample has been recovered. On the other hand, it is known(1,2,19) that the similar micelle is also formed from a solution of graft and block copolymers by preferentially decreasing the solvency of

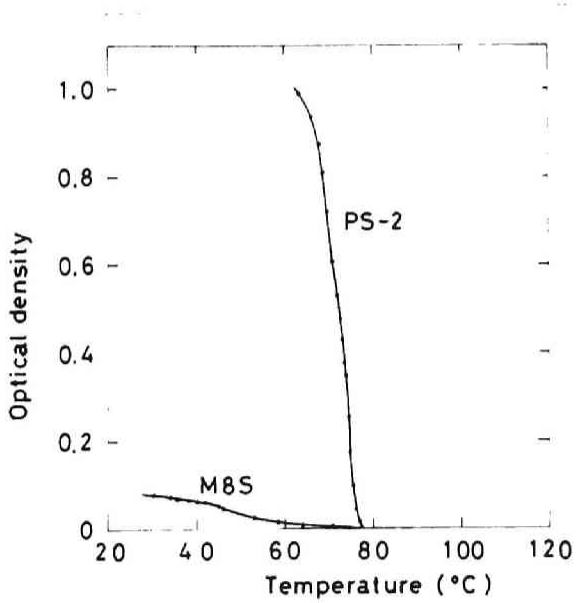
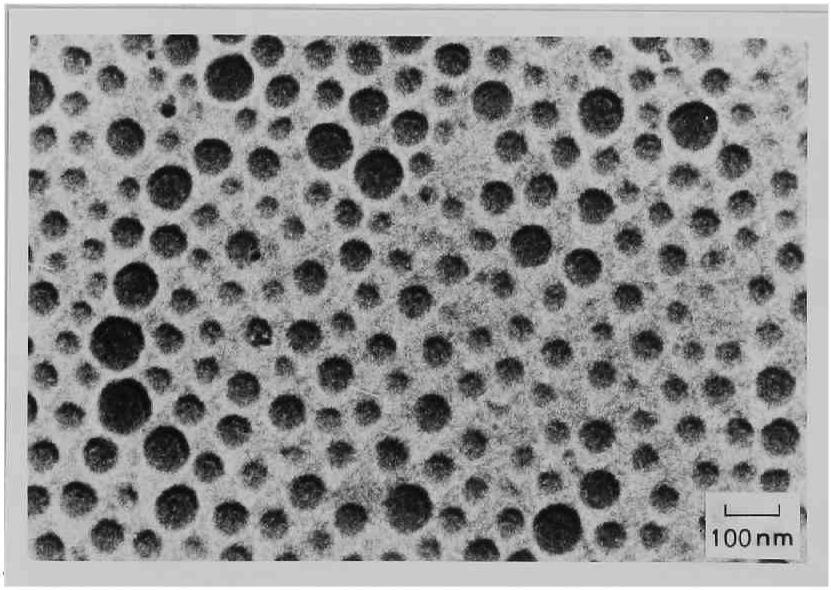


Fig. 9-1. Optical density-temperature curves of PVAC-styrene graft copolymer(M8S) and PS homopolymer(PS-2) in ethyl acetoacetate($c_{PS} \fallingdotseq 5$ mg/dl).

the medium for either of sequences, for example, by addition of a selective non-solvent to the solution. In the present work, single selective solvents were used instead of mixtures of good solvent and non-solvent to avoid the preferential solvation. The graft copolymer micelle was attempted to be formed by cooling the solution after the graft copolymer was completely dissolved once above T_θ of both sequences.

Fig. 9-1 shows typical examples of optical density-temperature curves of PVAC-styrene graft copolymer(M8S) and PS-2 in ethyl acetoacetate which is a θ-solvent for PS but a good solvent for PVAC. As clearly seen from Fig. 9-1, the turbidity of the graft copolymer solution increased very gradually, whereas that of the PS homopolymer solution with the same PS concentration appeared abruptly at a certain temperature and then rapidly increased. The turbidity of the graft copolymer solution kept at room temperature did not change at least for several months.

The electron micrographs taken from the solution exhibiting the constant turbidity are given in Fig. 9-2. The solvents used for the dialysis are good solvents for PVAC, but non-solvents for PS.



(a)

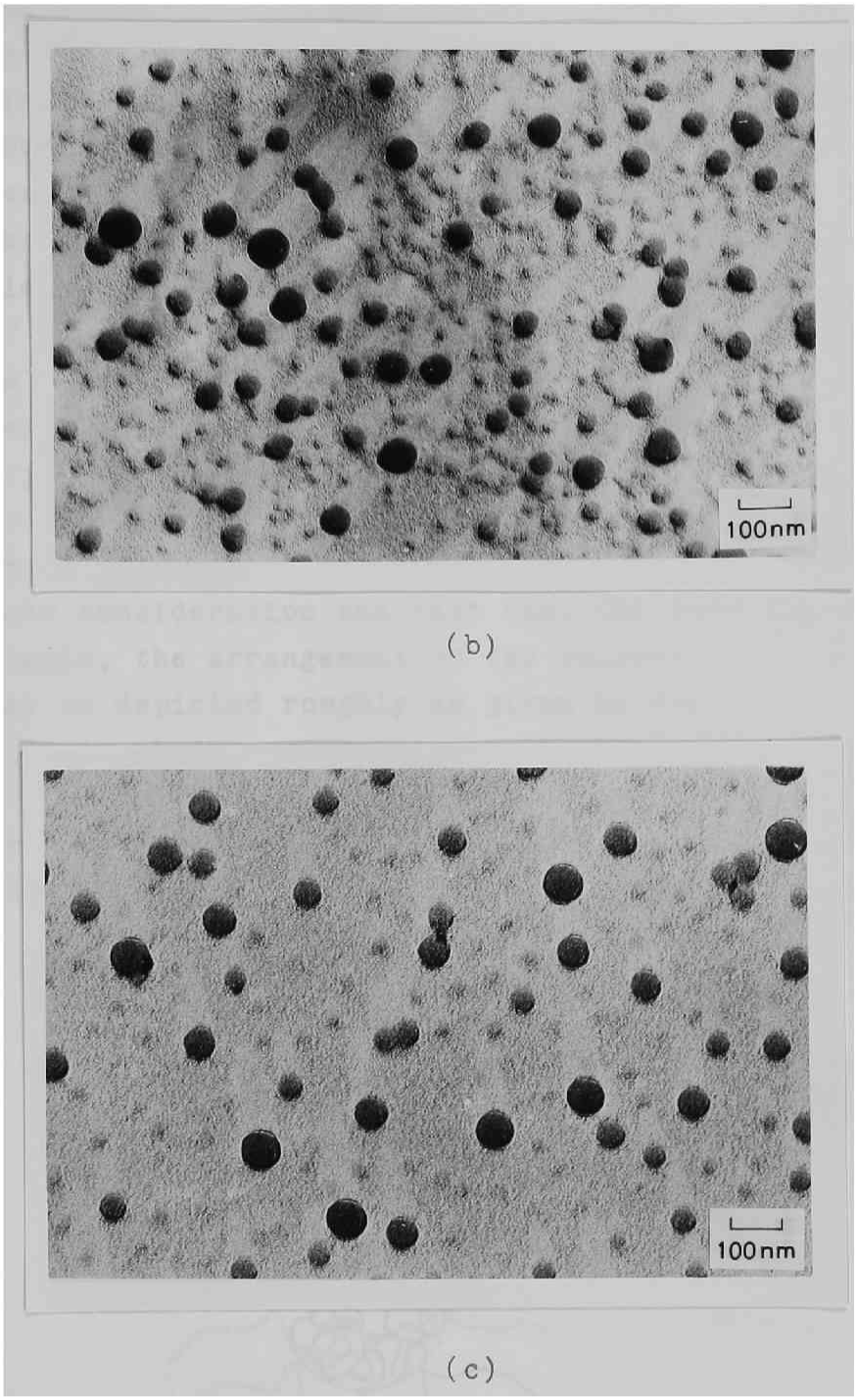


Fig. 9-2. Electron micrographs of micelles prepared from PVAC-styrene graft copolymer(M8S) in 1.0 g/dl solution of ethyl acetoacetate at room temperature: (a) not dialyzed ; (b) dialyzed against methanol ; (c) dialyzed against acetonitrile.

Clearly the dried micelles are spherical except for the undialyzed micelle of somewhat flattened structure. No difference is observed in the particle size between the two solvents for the dialysis. Further it was found that the initial polymer concentration influenced the particle size to an insignificant extent in the concentration range from 0.05 to 1.0 g/dl. The dispersity in particle sizes would be due to the dispersity in molecular weights of graft copolymer. From the average particle radius(ca. 300 Å) the number of graft copolymer molecules making up one micelle was found to be about 200 on the average, provided that the density is equal to that of the solid polymer (1.1 g/cm^3).

To give a plausible model about the inner structure of the micelle, more detailed information is needed. Nevertheless, if we take into consideration the fact that the spherical micelle is very stable, the arrangement of two polymer sequences in the micelle may be depicted roughly as given in Fig. 9-3. The insoluble and soluble chains construct the micelle core and the peripheral outer shell, respectively. Strictly speaking, the chains in the core of undried micelle are not in a fully precipitated, but in a highly concentrated phase, because the core part is

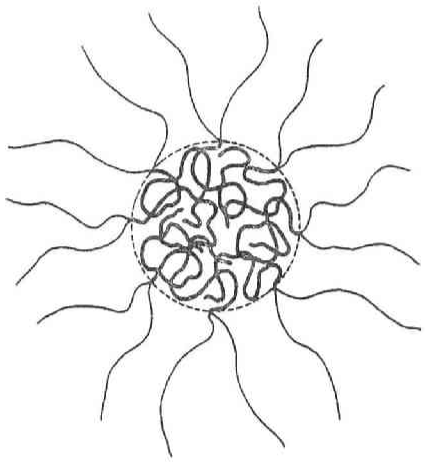


Fig. 9-3. A model of graft copolymer micelle.

formed as a consequence of the phase separation of the insoluble chain, which can be discussed similarly to that of the ordinary polymer-solvent two component systems(20).

2) Incipient cloud points of graft copolymers

As is seen in Fig. 9-1, the incipient cloud point(T_c) of the graft copolymer seems to be comparable to that of the corresponding homopolymer. In order to make this relationship in more detail, the subsequent experiments were carried out.

First the T_c values of PVAC-styrene graft copolymers and PS homopolymers were measured in ethyl acetoacetate at various concentrations. Fig. 9-4 shows plots of the reciprocal of T_c against the logarithm of the concentration of PS component c_{PS} (expressed as gram PS in 1 ml of the solution) according to the method proposed for homopolymers by Elias(21, 22) and Cornet and Ballegooijen (23). It is obvious that not only the PS homopolymers but also the graft copolymers satisfy a linear relationship between $1/T_c$ and log c_{PS}. The temperatures extrapolated to a pure polymer

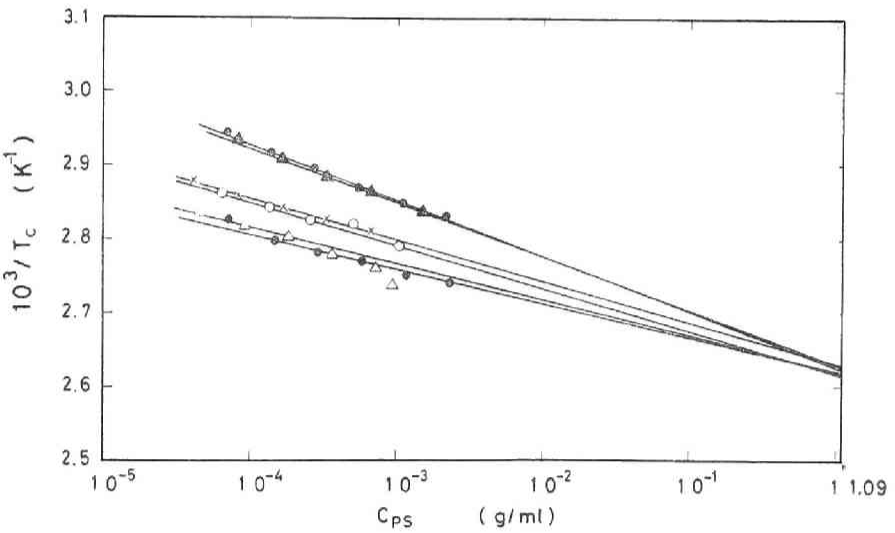


Fig. 9-4. Plots of the reciprocal of the incipient cloud point against the concentration of the PS component (PVAC-g-PS - ethyl acetoacetate) : (○) M8S ; (×) M9S ; (△) M10S ; (●) PS-1 ; (◉) PS-2 ; (▲) PS-4.

state where c_{PS} is equal to 1.09 g/ml, coincided fairly well with each other at 108.5 ± 1.0°C. It is interesting to note that the extrapolated temperature of a monodisperse PS-4(NBS 705) was in agreement with those of polydisperse PS.

According to Cornet et al., the extrapolated temperature, named a critical cloud point($T_{c,c}$), can be regarded as T_θ of the polymer. In fact the agreement between $T_{c,c}$ and T_θ is excellent for the PS homopolymer in diisobutyl ketone(DIBK) and the PMMA homopolymer in tetralin as will be described later (see Figs. 9-8 and 9-9). Therefore it follows that the T_c of the graft copolymer is equal to that of the corresponding homopolymer and in turn corresponds to that of the chain to be precipitated in the graft copolymer. Also in a solvent-precipitant system Climie and White(24) observed a similar phenomenon for polyacrylonitrile-PMMA block copolymers.

In addition, the T_c values of PVAC-styrene graft copolymers with one branch and PVAC homopolymers were measured in DIBK, where PVAC is precipitated at a higher temperature than PS. The result is shown in Fig. 9-5.

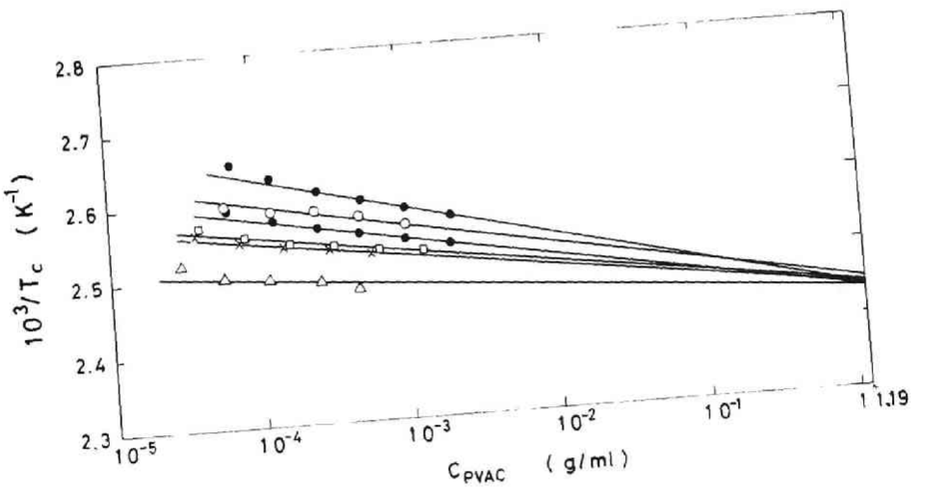


Fig. 9-5. Plots of the reciprocal of the incipient cloud point against the concentration of the PVAC component (PVAC-g-PS - DIBK) : (□) M3S ; (○) M8S ; (×) M9S ; (△) M10S; (●) PVAC-1 ; (●) PVAC-2.

As is clearly seen, the plot gives the same trend as in Fig. 9-4, the $T_{c,c}$ values being 136.5 ± 1.5 °C.

These results demonstrate that one sequence, i.e., either backbone or branch of the graft copolymer undergoes phase separation under the condition identical to that for the corresponding homopolymer, resulting in formation of the core of the micelle. Thus it may be concluded that the phase separation of the insoluble sequence in highly dilute solution is not influenced by the soluble sequence present in the same molecule, as far as the graft copolymer has a balanced structure. Besides, it will be noted that these graft copolymers with one branch do not form any monomolecular micelle even in very dilute solution as far as the solution temperature is below T_c of the insoluble chain. This is apparently in conflict with the statement of Sadron(25) that at very low concentration (less than 0.1 % in general) block copolymers are monomolecularly dispersed in selective solvents. The number of polymer chains constructing one micelle may be estimated by referring to the theories on the size of spherical domain in A-B block copolymers(26,27).

On the other hand, the values of T_c of PVAC-MMA graft copolymers with several branches shifted to lower temperatures as the number of branches increased (see Fig. 9-7). This may be explained by prevention of the branches for the aggregation of the backbone sequences. Gallot et al.(28) found that the graft copolymer with many branches was monomolecularly dispersed in a selective solvent(bad for backbone polymer).

3) Flocculation points of graft copolymer micelles

As is often pointed out, it is not easy to coagulate the graft copolymer micelle, once it is dispersed into a medium. For example, in the case shown in Fig. 9-1, no macroscopic phase separation took place even when a more concentrated solution was cooled to the freezing point of the solvent(- 45 °C). This finding seems to be characteristic for the graft copolymer behaving as an amphiphile. However, the micelle was found to become abruptly unstable as the solvency of the dispersion medium for the soluble chain was gradually decreased. Fig. 9-6 shows the optical

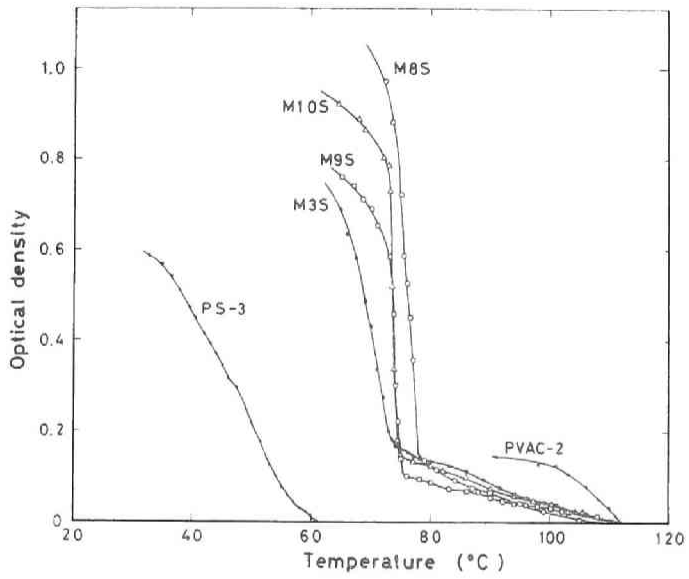


Fig. 9-6. Optical density - temperature curves of various polymers in DIBK ($c_{PVAC} \fallingdotseq 5$ mg/dl).

density - temperature curves of PVAC-styrene graft copolymers with one branch, a PVAC homopolymer and a PS homopolymer in DIBK, which is able to act as a θ-solvent for both homopolymers. The concentration of PVAC component was equal to that of the PVAC homopolymer. When the solutions of the graft copolymers were cooled below their T_c, the turbidities suddenly increased in every case at certain temperatures. These characteristic temperatures were much higher than the T_c of PS homopolymer, though its molecular weight was considerably higher than those of the branch PS. Clearly this abrupt, second increase of the turbidity should be attributed to the beginning of the flocculation of the graft copolymer micelle. Similar behavior was also observed in tetralin for PVAC-MMA graft copolymers with one or several branches, as shown in Fig. 9-7. In this solvent PVAC was precipitated at a higher temperature than PMMA.

Similarly to the study on T_c, the reciprocal of the incipient flocculation point(T_f) of the graft copolymer micelles was plotted against the logarithm of the concentration of the soluble

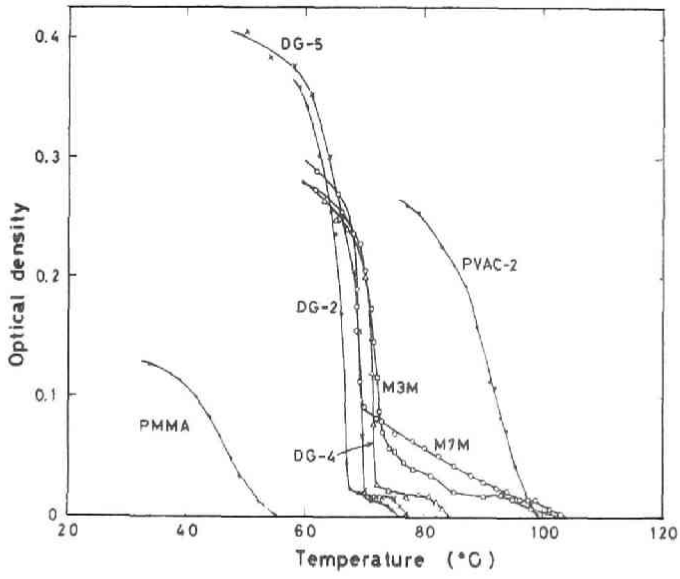


Fig. 9-7. Optical density - temperature curves of various polymers in tetralin ($c_{PVAC} \fallingdotseq 5$ mg/dl).

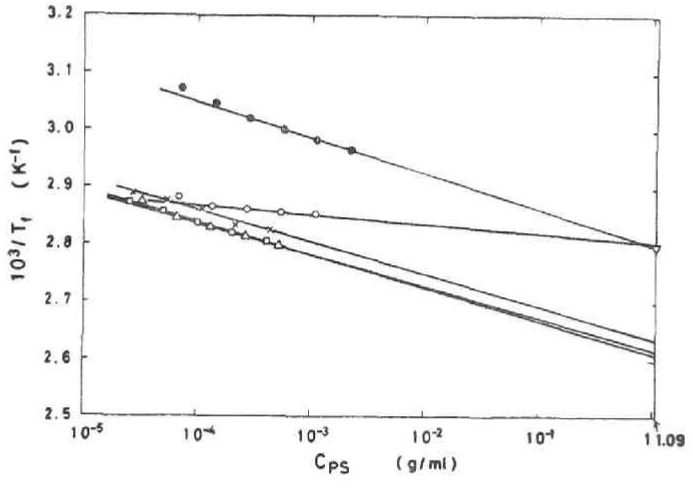


Fig. 9-8. Plots of the reciprocal of the flocculation point against the concentration of the PS component (PVAC-g-PS - DIBK) : (□) M3S ; (○) M8S ; (×) M9S ; (△) M10S ; (●) PS-2 ; (▽) T_θ of PS determined by osmometry.

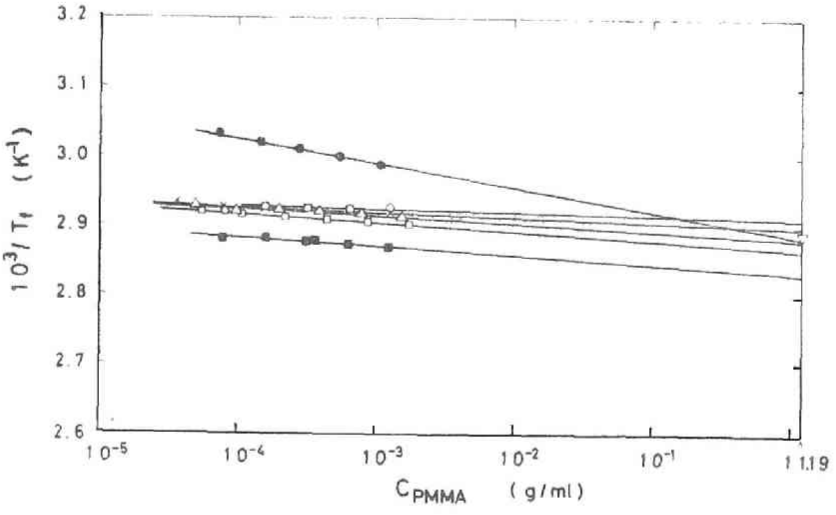


Fig. 9-9. Plots of the reciprocal of the flocculation point against the concentration of the PMMA component (PVAC-g-PMMA - tetralin) : (○) M3M ; (×) M7M ; (□) DG-2 ; (■) DG-4 ; (△) DG-5 ; (●) PMMA-1 ; (▽) T_θ of PMMA determined by osmometry.

polymer chain constructing the outer shell of micelle. The results of PVAC-styrene graft copolymers in DIBK and PVAC-MMA graft copolymers in tetralin are given, respectively, in Fig. 9-8 and 9-9, where the results of PS and PMMA homopolymers are also shown. As is seen, linear relationships hold in each case between $1/T_f$ and log c. Although there is no unambiguous theoretical reasoning for application of the Cornet's plot to the micelle flocculation, it is likely, at least, that the flocculation would be brought about at a higher temperature than that where the homopolymer corresponding to the outer shell initiates the phase separation. To eliminate the concentration effect we will use the extrapolated temperature, which is here defined as critical flocculation point($T_{f,c}$) and summarized in Tables 9-3 and 9-4.

Table 9-3. Critical flocculation temperatures of PVAC-styrene graft copolymers in DIBK.

		M3S	M8S	M9S	M10S
$10^3/T_{f,c}$	($^oK^{-1}$)	2.607	2.804	2.635	2.617
$T_{f,c}$	(^oC)	111	84	107	109

$T_{c,c}$ of PS-2 is 84 ^oC.
T_θ of PS is 84 ^oC.

Table 9-4. Critical flocculation temperatures of PVAC-MMA graft copolymers in tetralin.

		M3M	M7M	DG-2	DG-4	DG-5
$10^3/T_{f,c}$	($^oK^{-1}$)	2.910	2.895	2.865	2.830	2.880
$T_{f,c}$	(^oC)	71	73	76	80	74

$T_{c,c}$ of PMMA-1 is 74 ^oC.
T_θ of PMMA is 73 ^oC.

As is clear from the tables, $T_{c,c}$ of the homopolymer agrees quite well in both cases with T_θ determined osmometrically. On the other hand, the $T_{f,c}$ values of the graft copolymers are approximately equal to or higher than T_θ of the homopolymer. For instance, M10S gives $T_{f,c}$ higher than T_θ of PS by 25 ^oC. This suggests it to be possible that the graft copolymer micelles begin to be flocculated even in the dispersion medium of somewhat better solvency than the θ-solvent for the polymer forming the outer shell.

It is obvious that the motive force hindering the flocculation of micelles is not an electrostatic force. As many workers have pointed out(29-35), such nonionic polymeric dispersants are stabilized by the positive free energy change(chiefly negative entropy change) resulting from overlapping of the polymer chains in the outer shells. On the contrary, the attractive energy between the cores due to van der Waals force is much less than the energy of thermal motion unless the cores approach very closely to each other. Therefore this attractive force hardly affects the stability of the graft copolymer micelles.

On the other hand, it is reasonable to regard the micelle as the homopolymer with high molecular weight which is connected by the core. So the T_f, which are considered T_c of the high-molecular-weight "homopolymer", would be higher than T_c of the component homopolymer dissolving monomolecularly, but the $T_{f,c}$ would be close to the $T_{c,c}$(that is, T_θ). The trends shown in Figs. 9-8 and 9-9 can be understood by this model. It may be suggested that the deviation of $T_{f,c}$ from T_θ is due to the influence of the polymer forming the core on the solubility of the one forming the shell.

It can be said from the above result that the micelle emulsifying a large amount of the homopolymer shown in Chapter 7 and POO emulsion in Chapter 8 are also stabilized by the entropic repulsion resulting from overlapping of the polymer chains in the outer shells. With respect to the method to separate the pure graft copolymer from the corresponding homopolymers as mentioned in Chapter 6, the modified precipitation method is again confirmed to be very effective, since the graft copolymers are completely coagulated even in solvents of somewhat better solvency than θ-condition, whereas the corresponding homopolymers are of course still dissolved.

REFERENCES

1) H. A. J. Battaerd and G. W. Tregear, Graft Copolymers, Interscience, New York, 1967.
2) J. V. Dawkins, in Block Copolymers, D. C. Allport and W. H. Janes, Ed., Appl. Sci., London, 1973.
3) F. M. Merrett, Trans. Faraday Soc., 50, 759 (1954).
4) L. J. Hughes and G. L. Brown, J. Appl. Polymer Sci., 7, 59 (1963).
5) G. E. Molau, J. Polymer Sci., A, 3, 1267, 4235 (1965).
6) G. E. Molau, Kolloid-Z. Z. Polymere, 283, 493 (1970).
7) T. Okada, K. Yamazaki, and I. Sakurada, JAERI, 5027, 35 (1971).
8) Chapters 7 and 8.
9) J. D. Wellons, J. L. Williams, and V. Stannett, J. Polymer Sci., A-1, 5, 1341 (1967).
10) A. Banderet, C. Tournut, and G. Riess, in Macromolecular Chemistry, Prague, 1965 (J. Polymer Sci., C, 16), O. Wichterle and B. Sedlacek, Eds., Interscience, New York, 1967, p.2601.
11) G. Riess, J. Kohler, C. Tournut, and A. Banderet, Makromol. Chem., 101, 58 (1967).
12) J. Kohler, G. Riess, and A. Banderet, Europ. Polymer J., 4, 173 (1967).
13) T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, Macromolecules, 3, 87 (1970).
14) A. Skoulios, P. Helffer, Y. Gallot, and J. Selb, Makromol. Chem., 148, 305 (1971).
15) H. Bartl and W. v. Bonin, Makromol. Chem., 57, 74 (1962).
16) J. Periard, A. Banderet, and G. Riess, J. Polymer Sci., B, 8, 109 (1970).
17) J. Periard and G. Riess, Kolloid-Z. Z. Polymere, 248, 877 (1971).
18) P. A. Winsor, Chem. Rev., 68, 1 (1968).
19) T. Kotaka, T. Tanaka and H. Inagaki, Polym. J., 3, 327 (1972).
20) H. Tompa, Polymer Solution, Butterworths, London, 1956.
21) H. -G. Elias, Makromol. Chem., 33, 140 (1959).

22) H. -G. Elias, Makromol. Chem., 50, 1 (1961).
23) C. F. Cornet and H. V. Ballegooijen, Polymer, 7, 293 (1966).
24) I. E. Climie and E. F. T. White, J. Polym. Sci., 47, 149 (1960).
25) C. Sadron and B. Gallot, Makromol. Chem., 164, 301 (1973).
26) D. J. Meier, J. Polymer Sci. C, 26, 81 (1969).
27) T. Soen, T. Inoue, K. Miyoshi, and H. Kawai, J. Polymer Sci. A-2, 10, 1757 (1972).
28) Y. Gallot, E. Franta, P. Rempp, and H. Benoit, J. Polym. Sci. C, 4, 473 (1964).
29) E. W. Fischer, Kolloid-Z., 160, 120 (1958).
30) R. H. Ottewill and T. Walker, Kolloid-Z. Z. Polymere, 227, 108 (1968).
31) D. H. Napper, Trans. Faraday Soc., 64, 1701 (1968).
32) D. H. Napper, J. Colloid Interface Sci., 32, 106 (1970).
33) D. J. Meier, J. Phys. Chem., 71, 1861 (1967).
34) E. J. Clayfield and E. C. Lumb, J. Colloid Interface Sci., 22, 269, 285 (1966).
35) P. Bagchi and R. D. Vold, J. Colloid Interface Sci., 38, 652 (1972).

SUMMARY

Chapter 1. Introduction

Chapter 2. Comparison of True and Apparent Graft

When a grafting reaction of a monomer Y is carried out onto a polymer X, and the product is thoroughly extracted with a solvent for the polymer Y, the residue is conventionally called a graft; the weight increase in percent of the polymer X due to the unextractable polymer Y is regarded to be percent graft. However, it is possible that a part of polymer Y which is formed in the matrix of polymer X is unextractable due to occlusion by polymer X. When we determine the amount of polymer Y which is unextracted by the occlusion, we know the true value of the percent graft.

The grafting of methyl methacrylate(MMA) was carried out onto dry or water-swollen films of poly(vinyl alcohol) (PVA) in the presence of methanol mainly by a mutual irradiation technique and the true and an apparent percent graft were compared.

It was found that difference between the apparent percent graft (A) and the true one (B) was considerably large, the fraction of true graft (B/A) ranging from 0.02 to 0.57. The true percent graft and the branch length were also discussed in dependence on the methanol content of the monomer mixture and the degree of water-swelling of the films.

Chapter 3. Solvent Effects on Radiation Graft Copolymerization

The radiation graft copolymerization of styrene or MMA onto PVA films was carried out in the presence of swelling agents such as methanol and water. Basing on the variation of total conversion, weight increase and molecular weight of the polymer formed, effects of the swelling agents on the grafting were discussed. In addition, the investigation was extended to the grafting systems containing a small amount of chain transfer agents. It was found that methanol has several effects on the heterogeneous grafting other than to accelerate the diffusion of monomer into

the substrate matrix. In the grafting of styrene methanol caused an appreciable gel effect, while it behaved as a simple diluent in the grafting of MMA. The chain transfer agents reduced the yield as well as the length of the polymer formed in the film, the chain transfer constant being in agreement with that formed in the conventional catalytic homopolymerization. The number of grafted branches was not affected by the presence of the chain transfer agent.

Chapter 4. Chemical Structure of Poly(Vinyl Alcohol)-Methyl Methacrylate Graft Copolymers Prepared by Various Methods

PVA-MMA graft copolymers were prepared by a mutual irradiation, pre-irradiation, and catalytic method with potassium persulfate(KPS); a technique to prepare graft copolymer using no initiator was also adopted. After pure graft copolymers were isolated from the grafted products by the vigorous alternate extraction of unreacted PVA and homoPMMA, hydroxyl groups in the copolymers were completely acetylated to carry out osmotic pressure measurements and determine the chemical composition by hydrolysis. Grafted branches were separated by cleaving C-C bonds of 1,2-glycol structure in backbone PVA with periodic acid. The chemical structure of the graft copolymers was made clear on the basis of the measured number-average molecular weights of the pure graft copolymer, separated branch and mother PVA molecule, and the chemical composition of the graft copolymer. It was found that the graft copolymer has only one branch and one mother PVA molecule, irrespective of the grafting methods employed.

Chapter 5. Comparison of Theoretical and Experimental Results on Yield and Chemical Structure of Graft Copolymers in Radiation Grafting

Fundamental quantities in the grafting such as the fraction of the mother polymer participating in the grafting and the number of branches formed were calculated as a function of the

probability of branch formation from the monomer residue of the mother polymer. The theoretical results indicated that the yield and the chemical structure of graft copolymers can be evaluated by the G_b-value of the branch formation, defined as the number of branches formed per 100 eV radiation energy. On the other hand, the experimental results showed that the G_b-value was almost equivalent to the G_R-value of radical formation on mother polymer. Therefore it seems possible to roughly predict the above fundamental quantities on the basis of the G_R-value. The graft copolymer with two branches on the average can be produced if the weight fraction of mother polymer grafted becomes higher than 0.75, which is, however, hardly attainable at the usual radiation grafting. Some attempts to increase the number of the branches were also described.

Chapter 6. Isolation of Graft Copolymer from the Reaction Product

Some problems on the isolation of graft copolymers from their reaction products by selective precipitation, extraction, and column chromatography methods were discussed and the result on estimation of the purity of graft copolymers by thin-layer chromatography was given. It was found that the graft copolymer produced can emulsify the coexisting homopolymers, resulting in disturbance of the removal of the homopolymers. However, pure graft copolymers can be isolated relatively easily, if one tries to remove the homopolymers not in the emulsified nor collapsed state, regardless of the isolation methods employed. Column adsorption chromatography seems to be the most rapid and simple method of the three. It was also clarified that the thin-layer chromatography can detect the homopolymers contaminating to the extent as low as 0.5-1.0%.

Chapter 7. Emulsifying Effect of Graft Copolymer for the Homopolymer

Precipitation of homoPMMA from dimethyl sulfoxide solution by addition of water as a precipitant was studied in the presence of a well-characterized graft copolymer of PVA. The graft copoly-

mer which had been prepared by a radiation method and freed from homoPMMA and homoPVA had one PMMA branch whose length was nearly equal to that of the PVA backbone. Even when such an amount of water was added to PMMA solution as to cause all the PMMA to precipitate from the solution, the precipitation was prevented by the presence of relatively small amounts of the graft copolymer. With decreasing molecular weight of PMMA, the effect of protection became more pronounced. When the precipitation was prevented, the solution was transformed into a stable emulsion. The mechanism of protection against precipitation was discussed on the basis of the results obtained and electron microscopic photographs of the emulsion particles. It was concluded that the particles of the precipitated homopolymer were covered by a monolayer of the graft copolymer, resulting in prevention of coagulation.

Chapter 8. Effect of Graft Copolymer on Demixing of Immiscible Polymers in Solution

The effect of graft copolymer on the demixing of solutions of two immiscible homopolymers and critical conditions for emulsion formation were studied. The graft copolymer used in the present work consists of one backbone PVAC and one branch PS. PVAC and PS of various degrees of polymerization were used as immiscible homopolymers. The common solvent was benzene. When the concentration of homopolymer blend was not sufficiently higher that the critical concentration for demixing of the blend solution, no stable emulsion was formed, even when a considerable amount of graft copolymer was present, and the added graft copolymer merely reduced the demixing rate. However, as the blend concentration was increased, a stable emulsion could readily be obtained by addition of rather small amounts of graft copolymer. The radius of emulsion droplets was inversely proportional to the weight ratio of the graft copolymer to the dispersed component polymer, in accordance with a theoretical prediction. It was concluded that the emulsions were stabilized against coagulation by graft copolymer molecules fixed strongly as a monolayer on the interface of emulsion.

Chapter 9. The Formation and Flocculation of Graft Copolymer Micelles

In order to clarify the aggregation process of graft copolymers as amphiphilic compounds, the conditions of the formation and flocculation of micelles in single selective solvents from pure graft copolymers were investigated by turbidimetry. Two series of graft copolymers from PVAC were used; PVAC-styrene graft copolymers with one branch and PVAC-MMA graft copolymers with one or several branches. These graft copolymers could be completely coagulated through the two processes in the selective solvents which were θ-solvents common to both sequences but had widely different θ-temperatures. The first process is the formation of micelle. One sequence of the graft copolymers became desolvated under the same condition as the corresponding homopolymers, resulting in formation of the core of the micelle. Another, still soluble sequence may extend from the surface of the core into a solvent phase, covering the outer shell of the micelle. Therefore no macroscopic phase separation occurred and a stable dispersion was formed. The second process is that the micelle became too unstable to exist as dispersed, as the solvency of the medium for the soluble sequence was decreased. As a result the coagulation of the micelle took place finally.

LIST OF PUBLICATIONS

Chapter 2. Makromol. Chem., 139, 171 (1970).

Chapter 3. Bull. Inst. Chem. Res., Kyoto Univ., 46, 13 (1968); ibid., 49, 6 (1971); ibid, 52, 318 (1974).

Chapter 4. Makromol. Chem., 139, 183 (1970).
Bull. Inst. Chem. Res., Kyoto Univ., 47, 58 (1969).

Chapter 5. Makromol. Chem., 175, 227 (1974).

Chapter 6. J. Polym. Sci., Polym. Letters Ed., 12, 27 (1974).

Chapter 7. J. Polym. Sci., Polym. Chem. Ed., 11, 27 (1973).
Bull. Inst. Chem. Res., Kyoto Univ., 50, 27 (1972).

Chapter 8. J. Polym. Sci., Polym. Chem. Ed., 11, 41 (1973).

Chapter 9. J. Polym. Sci., Polym. Chem. Ed., 12, 323 (1974).

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